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STRUCTURE OF HALOGENATES OF THE TYPE $A(BO_3)_2 \cdot H_2O$

Part II. Barium Bromate Monohydrate $Ba(BrO_3)_2 \cdot H_2O$

By Gopinath Kartha

(*Department of Physics, Indian Institute of Science, Bangalore-3*)

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

Introduction

In a previous communication to these *Proceedings* (Kartha, 1952; referred to here as (I)) the details of the structure analysis and the atomic co-ordinates of one of the members of the isomorphous series of halogenate crystals $A(BO_3)_2 \cdot H_2O$, *viz.*, barium chlorate monohydrate have been reported. In continuation of these studies, the author has investigated the structure of the crystal of barium bromate monohydrate which is also isomorphous with the above series and the results are presented in this paper.

2. Morphological Studies

Barium bromate, which is only very slightly soluble in water at room temperature, was precipitated from an aqueous solution of barium chloride by the addition of potassium bromate solution. The precipitate, which was in the form of a white powder, was washed repeatedly in warm water to remove traces of the other salts which were much more soluble than barium bromate. The final precipitate was dissolved in warm water and allowed to crystallize.

The crystals were found to be tabular in form with the *m* planes (110) most prominent. Since the results of goniometric measurements as given by different authors (Groth, 1908) were found to be different, a re-examination of the morphological data was made using a two circle optical goniometer. The measurements of the present author gave axial ratios $a:b:c = 1{\cdot}146 : 1 : 1{\cdot}215$ and these are more in accordance with those of Marignac than of either Rammelsberg or Epples. The monoclinic angle was found to be 93° 5′.

3. Unit Cell and Space Group

Rotation and oscillation photographs about the crystallographic axes gave the values

$$a = 9{\cdot}1\,\text{Å},\ b = 8{\cdot}0\,\text{Å} \text{ and } c = 9{\cdot}7\,\text{Å}$$

for the unit cell. More accurate measurements of the high order reflections from Weissenberg photographs gave the following values for the cell dimensions

$$a = 9{\cdot}06\,\text{Å},\ b = 7{\cdot}92\,\text{Å},\ \text{and}\ c = 9{\cdot}66\,\text{Å}.$$

These gave the axial ratios $a : b : c = 1{\cdot}144 : 1 : 1{\cdot}219$ in good agreement with the morphological data. Taking the value 3·99 (*Handbook of Physics and Chemistry*, 1948) for the specific gravity of barium bromate crystals, the number of molecules per unit cell works out to be 3·95, *i.e.*, $Z = 4$.

From zero-level and first-level Weissenberg photographs the following systematic extinctions were observed:

Reflections *hkl* absent if $h + k + l$ is odd

and *h*0*l* absent if either h or l is odd.

Because the crystal belongs to the monoclinic prismatic class, the only possible space group is C_{2h}^6 in the configuration I 2/*c*. As in the case of barium chlorate monohydarte, this could be put in the standard form C 2/*c* as given in the *International Tables* by a suitable transformation of axes. However, the former configuration is more suitable for the purpose of structure analysis.

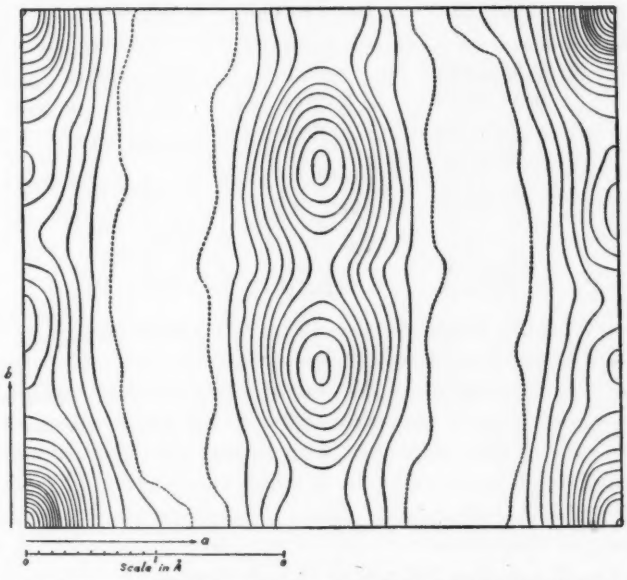
4. X-RAY DIFFRACTION DATA

Since the linear absorption co-efficient of the crystal is large (185 cm.$^{-1}$) even for Mo Kα radiation, a very small cylindrical crystal of about 0·1 mm. radius was used in obtaining the *c*-axis Weissenberg photographs for the purpose of making intensity estimates. As in the case of barium chlorate monohydrate, here also the diffraction spots were recorded by the multiple film method of Robertson (1943) using three films interleaved with silver foils. The intensities were estimated by visual comparison of the diffraction spots in all the three films with standard intensity marks. Since the crystal was used after being ground to the form of a cylinder, absorption corrections were made following the method of Bradley (1935) for cylindrical Debye-Scherrer specimens. Lorentz and polarization corrections were made using the tables of Buerger and Klein (1945) for zero-level normal beam photographs and using the chart of Cochran (1948) for the higher level layers, which were recorded by the equi-inclination method. The scale and temperature factors were obtained using the method of Wilson (1942).

5. THE *c*-AXIS PATTERSON AND FOURIER PROJECTIONS

The symmetries and point positions for the unit cell of barium bromate monohydrate are, of course, the same as those for barium chlorate

monohydrate and they have been given in (I). Using the *hk*0 reflections, a Patterson projection was made and this is shown in Fig. 1.



Barium bromate, The (001) Patterson projection. Contours at intervals of 8 on an arbitrary scale dotted lines denote 0

FIG. 1

It is seen that the positions of all the important peaks could be explained by assuming that the atomic positions in the *c*-projection are approximately the same as in barium chlorate (I) even though the heights of the peaks suggest that an atom of much higher scattering power occupies the position of the chlorine atom. The various important peaks in the projection could be designated as shown in Table I.

However, the elongation of the Br-Br peaks along the *b*-axis suggests that in this case, the bromines, unlike the chlorines in the case of the chlorate, do not exactly overlap at (0·25, 0·25), in the *c*-projection but have slightly different *b*-co-ordinates.

Since the Patterson projection shows that to a first approximation the atomic co-ordinates of barium and halogens are the same both for the chlorate and bromate crystals, we see that the bromine contribution is zero for those *hk*0 reflections for which *h* is odd. Hence, we can assume that for these reflections the phase is entirely fixed by the sign of the barium

TABLE I

Patterson Peaks in Barium Bromate Monohydrate

Position	Value of peak	Designation
0·00, 0·00 0·50, 0·50	580 580	All vectors (γ—S)
0·50, 0·00 0·00, 0·50	378 378	16 (Br—Br)
0·00, 0·20	211	2 (Ba—Ba)
0·00, 0·15	308	8 (Br—Ba)
0·50, 0·15 0·00, 0·15	180 180	16 (Br—O)
0·24, 0·00	146	8 (Ba—O)

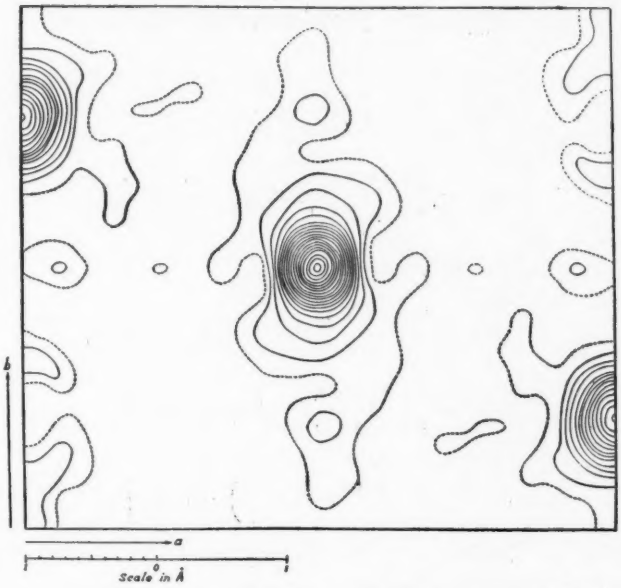
contribution. In fact, the absolute structure amplitudes of barium chlorate and barium bromate are very nearly the same for these reflections. However, in the case of $hk0$ reflections with h even the eight bromine atoms make their full contribution, the sign of which is positive if $\frac{1}{2}(h+k)$ is even and negative if $\frac{1}{2}(h+k)$ is odd. Since $2f_{Br}$ is always greater than f_{Ba} we could assume that the sign is fixed by the bromine contribution for these reflections, *i.e.*, if h is even, the sign of F_{hk0} is positive or negative depending on whether $\frac{1}{2}(h+k)$ is even or odd respectively. Using the phases of reflections obtained in this way, a Fourier projection was made on the $a-b$ plane and this is shown in Fig. 2.

From Fig. 2 it is seen that in its main outlines this projection resembles the c-axis Fourier projection of barium chlorate monohydrate (I). However, the atomic positions of bariums are slightly different and the peak at (0·25, 0·25) due to overlap of two bromine atoms is more elongated in the projection. To obtain further information we have to refine the atomic co-ordinates and remove the diffraction effects around the heavy atoms. This is considered in the next section.

6. THE REFINEMENT OF ATOMIC CO-ORDINATES

The co-ordinates of the barium atoms were refined by the method of differential synthesis suggested by Booth (1946). The electron density distribution $\sigma(x, y)$ in the c-projection is represented by

$$\sigma(x, y) = \frac{1}{A}\sum_h\sum_k \left| F_{hk0} \right| \cos 2\pi \left[\left(h\frac{x}{a} + k\frac{y}{b}\right) - \alpha_{hk0}\right] \qquad (1)$$



BARIUM BROMATE THE FIRST FOURIER PROJECTION ON (001). CONTOURS AT INTERVAL OF 10 e Å^{-2}
THE DOTTED LINES DENOTE 10 e Å^{-2}

FIG. 2

where A is the area of the projected unit cell. Since at the position (x_r, y_r) of maximum electron density distribution we have the conditions

$$\left(\frac{\partial\sigma}{\partial x}\right)_{x=x_r} = \left(\frac{\partial\sigma}{\partial y}\right)_{y=y_r} = 0 \tag{2}$$

we get from (1) and (2)

$$-\frac{2\pi}{Aa}\sum_h\sum_k h\left|F_{hk0}\right|\sin 2\pi\left[\left(h\frac{x_r}{a}+k\frac{y_r}{b}\right)-\alpha_{hk0}\right]=0 \tag{3}$$

$$-\frac{2\pi}{Ab}\sum_h\sum_k k\left|F_{hk0}\right|\sin 2\pi\left[\left(h\frac{x_r}{a}+k\frac{y_r}{b}\right)-\alpha_{hk0}\right]=0$$

If the electron density maximum, instead of being at (x_r, y_r) is actually at $(x_r + \epsilon_r{}^x, y_r + \epsilon_r{}^y)$ where ϵ is small, we get from (3) the two linear

$$\begin{aligned} A_{hh}\,\epsilon_r{}^x + A_{hk}\,\epsilon_r{}^y + A_h &= 0 \\ A_{kh}\,\epsilon_r{}^x + A_{kk}\,\epsilon_r{}^y + A_k &= 0 \end{aligned} \tag{4}$$

where

$$A_{hh} = \frac{4\pi^2}{Aa^2} \sum_h \sum_k h^2 \left| F_{hk0} \right| \cos \theta$$

$$A_{hk} = \frac{4\pi^2}{Aab} \sum_h \sum_k hk \left| F_{hk0} \right| \cos \theta$$

$$A_h = \frac{2\pi}{Aa} \sum_h \sum_k h \left| F_{hk0} \right| \sin \theta$$

$$A_{kh} = A_{hk}$$

$$A_{kk} = \frac{4\pi^2}{Ab^2} \sum_h \sum_k k^2 \left| F_{hk0} \right| \cos \theta$$

$$A_k = \frac{2\pi}{Ab} \sum_h \sum_k k \left| F_{hk0} \right| \sin \theta$$

$$\theta = 2\pi \left[\left(h \frac{x_r}{a} + k \frac{y_r}{b} \right) - \alpha_{hk0} \right] \qquad (5)$$

Assuming the barium co-ordinates (x_r, y_r) to be $(0{\cdot}000\,a,\ 0{\cdot}400\,b)$, we could evaluate the quantities A_{hh}, A_{hk}, etc., of (5) and substituting these values in (4) solve for the corrections $\epsilon_r{}^x$ and $\epsilon_r{}^y$ for the barium atom. Using the data given by the $hk0$ reflections the values of ϵ^x and ϵ^y for the barium atom were calculated to be

$$\epsilon_{Ba}{}^y = -\,0{\cdot}009\,b \text{ and } \epsilon_{Ba}{}^x = 0{\cdot}0008\,a$$

giving the refined parameters

$$x_{Ba} = 0{\cdot}0008\,a \text{ and } \quad y_{Ba} = 0{\cdot}391\,b.$$

Since the space group demands that the x-co-ordinates of the barium atom be zero, we get the final values (0·000, 0·391) for the barium co-ordinates.

It was not possible to refine the bromine co-ordinates (0·25, 0·25) by the method of differential synthesis for the following reasons. Firstly, (0·25, 0·25) being a center of inversion, a continuous function can have a maximum at $(0{\cdot}25 + \epsilon^x,\ 0{\cdot}25 + \epsilon^y)$ only if ϵ is zero, for, otherwise the function will have two maxima having an infinitesimal separation of 2ϵ along the co-ordinate axes. As this is not possible for a continuous function there could be only one maximum corresponding to the value $\epsilon = 0$ in these cases. Secondly, due to overlap of the two bromine atoms in this region

the actual maximum could be expected to give, not the electron density maximum of either atoms separately, but only that of the combined distribution. However, the first difficulty could be got over by using co-ordinates slightly different from (0·25, 0·25) as the starting point for the refinement. By refining the barium positions by minimization methods, where our knowledge of the electron density distribution around each atom separately could be used, the second difficulty could be overcome.

For refinement of the y-co-ordinates the function

$$R = \Sigma | | RF_0 | - | F_c | |$$

was minimised by Southwell's relaxation method. Since the contribution of the bromine atoms at (x_r, y_r) to the reflection $hk0$ is $8 f_{Br} \cos 2\pi h x_r \cos 2\pi k y_r$ the condition of minimization of R gave the expression for the refinement $\epsilon_{Br}{}^y$ as

$$\epsilon_{Br}{}^y = - R \Big/ \frac{\partial R}{\partial y_{Br}} \tag{6}$$

where

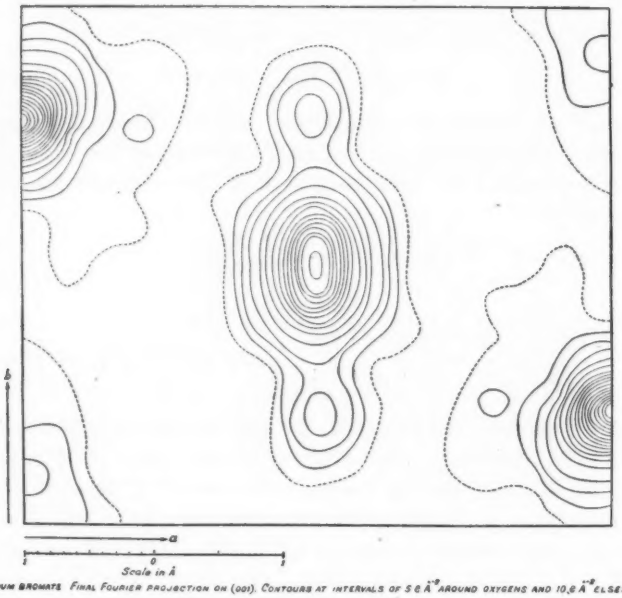
$$\frac{| | F_0 | - | F_c | |}{| F_0 | - | F_c |} \frac{\partial R}{\partial y_{Br}} = \frac{16\pi}{b} \sum_h \sum_k k f_{Br} \cos 2\pi h \frac{x_r}{a} \sin \left(2\pi k \frac{y_r}{b} - a_{hk0} \right) \tag{7}$$

Assuming that the values (x_r, y_r) for the bromine atoms are (0·250 a, 0·245 b) the correction $\epsilon_{Br}{}^y$ was obtainedand the value of R re-calculated using the corrected co-ordinates. Since the value of R thus calculated was actually greater than R before refinement and the correction ϵ was comparatively large, the method suggested by Booth (1949) for such cases was adopted. For this, the correction ϵ was scaled down to 0·1 Å and the three R values R_0, R_1 and $R_{\frac{1}{2}}$, corresponding to the three values (x_r, y_r), $(x_r, y_r + \epsilon_r)$ and $(x_r, y_r + \epsilon_r/2)$ for the barium co-ordinates, are obtained. If the curve of descent is assumed to be parabolic in nature it is easily shown that the correction $\epsilon_{min.}$ corresponding to the minimum of the function R is given by

$$\epsilon_{min} = (3 R_0 + R_1 - 4 R_{\frac{1}{2}}) / 4 (R_0 + R_1 - 2 R_{\frac{1}{2}}) \tag{8}$$

The co-ordinates of bromine and barium as well as the scale factor of the reflections were refined by this method. During the process of refinement, the reliability index R reduced from 0·33 to 0·17; the latter corresponding to the final co-ordinates (0·000, 0·391) and (0·250, 0·227) for the barium and bromine atoms respectively. It is interesting to note that this method also led to the same refined value 0·391 for the y-co-ordinate of barium as the differential synthesis method.

As explained in the case of barium chlorate monohydrate (I), a Fourier projection along *c*-axis free from diffraction effect was obtained by extending the series using the F_{hk0} values calculated from the bromine and barium contributions which are accurately known. The final projection thus obtained is shown in Fig. 3.



BARIUM BROMATE. FINAL FOURIER PROJECTION ON (001). CONTOURS AT INTERVALS OF 5 e.Å^{-2} AROUND OXYGENS AND 10 e.Å^{-2} ELSEWHERE. THE DOTTED CONTOUR REPRESENTS 5 e.Å^{-2}

FIG. 3

Space group considerations fixed the *c*-co-ordinate of barium as 0·250. However, the *c*-co-ordinate of bromine is variable and this was refined by the above method using the *hkl* reflections and was finally fixed at 0·550. Since the oxygen positions could not be fixed with much accuracy due to the comparatively small scattering power of these atoms, their co-ordinates were assumed to be not much different from those in barium chlorate monohydrate in evaluating the minimization functions.

7. ATOMIC CO-ORDINATES AND DISCUSSION

The atomic co-ordinates of barium bromate monohydrate, both fractional and Ångstroms are given in Table II.

TABLE II

Atomic Co-ordinates of Barium Bromate Monohydrate

Atom	Fractional			Ångstroms		
	u	*v*	*w*	*x*	*y*	*z*
Barium ..	0·000	0·391	0·250	0·00	3·13	2·42
Bromine ..	0·250	0·227	0·550	2·27	1·82	5·31
Oxygen 1 ..	0·09	0·34	0·56	0·8	2·7	5·4
Oxygen 2 ..	0·25	0·10	0·66	2·3	0·8	6·3
Oxygen 3 ..	0·27	0·23	0·40	2·4	1·8	3·8
Water Oxygen ..	0·00	0·06	0·25	0·0	0·5	2·4

As already mentioned, much accuracy is not claimed for the co-ordinates of the oxygen atoms. In Table III are given the observed and calculated structure amplitudes of the *hkO* and *hk*1 reflections.

TABLE III

Observed and Calculated Structure Amplitude of Barium Bromate Monohydrate

h	*k*	*l*	F_o	F_0	*h*	*k*	*l*	F_o	F_0
0	0	0	736	..	3	1	0	−103	89
0	2	0	−206	172	3	3	0	62	60
0	4	0	−15	<10	3	5	0	103	87
0	6	0	−140	172	3	7	0	−15	<15
0	8	0	71	58	3	9	0	−48	43
0	10	0	36	31	3	11	0	−12	14
1	1	0	−160	170	4	0	0	400	483
1	3	0	135	110	4	2	0	−111	124
1	5	0	104	118	4	4	0	−18	<10
1	7	0	7	25	4	6	0	−119	122
1	9	0	−54	45	4	8	0	60	52
1	11	0	11	<15	4	10	0	35	35
2	0	0	−88	51	5	1	0	−81	69
2	2	0	264	295	5	3	0	43	35
2	4	0	−260	225	5	5	0	84	85
2	6	0	35	25	5	7	0	3	<10
2	8	0	15	16	5	9	0	−51	44
2	10	0	27	30	5	11	0	−8	<15

TABLE III—(*Contd.*)

h	*k*	*l*	F_c	F_o	*h*	*k*	*l*	F_c	F_o
6	0	0	−68	75	17	1	0	−9	<15
6	2	0	160	154	17	3	0	5	<15
6	4	0	−157	145	17	5	0	9	15
6	6	0	10	25	0	1	1	−54	..
6	8	0	23	<10	0	3	1	−163	215
7	1	0	−60	60	0	5	1	42	34
7	3	0	30	25	0	7	1	63	57
7	5	0	71	63	1	0	1	0	<20
7	7	0	−10	15	1	2	1	231	224
7	9	0	−38	26	1	4	1	−38	40
8	0	0	211	218	1	6	1	4	20
8	2	0	−71	59	1	8	1	−96	132
8	4	0	−1	30	1	10	1	81	66
8	6	0	−77	79	2	1	1	154	246
8	8	0	40	47	2	3	1	−135	146
9	1	0	−56	53	2	5	1	−28	<20
9	3	0	40	23	2	7	1	108	111
9	5	0	47	60	2	9	1	10	<20
9	7	0	−4	15	2	11	1	−37	31
9	9	0	−31	−37	3	0	1	0	<20
10	0	0	−8	<10	3	2	1	77	143
10	2	0	67	65	3	4	1	129	109
10	4	0	−93	73	3	6	1	−160	176
10	6	0	12	22	3	8	1	21	<20
11	1	0	−37	32	3	10	1	−20	<20
11	3	0	25	21	4	1	1	−21	70
11	5	0	36	30	4	3	1	−139	137
11	7	0	−10	<15	4	5	1	43	30
11	9	0	−16	17	4	7	1	52	30
12	0	0	100	73	4	9	1	8	<20
12	2	0	−33	29	5	0	1	0	<20
12	4	0	−5	26	5	2	1	169	165
13	1	0	−27	19	5	4	1	−35	42
13	3	0	18	19	5	6	1	1	<20
13	5	0	22	20	5	8	1	115	78
13	7	0	−1	<15	6	1	1	−138	133
14	0	0	−5	26	6	3	1	−76	77
14	2	0	32	23	6	5	1	1	<20
14	4	0	−39	33	6	7	1	81	61
15	1	0	−13	17	7	0	1	0	<20
15	3	0	6	15	7	2	1	60	69
15	5	0	17	16	7	4	1	69	86
16	0	0	35	24	7	6	1	−119	111
16	2	0	−11	15	7	8	1	23	<20
16	4	0	0	<10	7	10	1	−18	<20

TABLE III—(*Contd.*)

h	*k*	*l*	F_c	F_0	*h*	*k*	*l*	F_c	F_0
8	1	1	−25	<20	3	8	$\bar{1}$	−106	111
8	3	1	−90	78	4	1	$\bar{1}$	−86	<20
8	5	1	41	30	4	3	$\bar{1}$	−134	154
8	7	1	26	33	4	5	$\bar{1}$	57	<20
9	0	1	0	<20	5	0	$\bar{1}$	0	<20
9	2	1	97	79	5	2	$\bar{1}$	68	84
9	4	1	−21	<20	5	4	$\bar{1}$	81	103
9	6	1	−60	71	5	6	$\bar{1}$	−150	118
10	1	1	−68	55	6	1	$\bar{1}$	−107	171
10	3	1	−38	42	6	3	$\bar{1}$	−85	55
10	5	1	−4	23	6	5	$\bar{1}$	3	<20
10	7	1	44	49	6	7	$\bar{1}$	79	77
11	0	1	0	<20	7	0	$\bar{1}$	0	<20
11	2	1	24	34	7	2	$\bar{1}$	119	134
11	4	1	41	52	7	4	$\bar{1}$	−15	<20
11	6	1	−59	71	7	6	$\bar{1}$	−5	<20
12	1	1	−2	<20	7	8	$\bar{1}$	−81	81
12	5	1	−42	49	8	1	$\bar{1}$	−22	<20
1	0	$\bar{1}$	0	<20	8	3	$\bar{1}$	−78	88
1	2	$\bar{1}$	74	86	8	5	$\bar{1}$	19	<20
1	4	$\bar{1}$	125	149	9	0	$\bar{1}$	0	<20
1	6	$\bar{1}$	−182	192	9	2	$\bar{1}$	27	43
2	1	$\bar{1}$	−208	234	9	4	$\bar{1}$	53	30
2	3	$\bar{1}$	−153	113	9	6	$\bar{1}$	−72	81
2	5	$\bar{1}$	15	23	10	1	$\bar{1}$	−50	85
2	7	$\bar{1}$	93	79	10	3	$\bar{1}$	−43	<20
3	0	$\bar{1}$	0	<20	11	0	$\bar{1}$	0	<20
3	2	$\bar{1}$	196	178	11	2	$\bar{1}$	62	63
3	4	$\bar{1}$	−53	<20	12	1	$\bar{1}$	−16	<20
3	6	$\bar{1}$	−9	<20	12	3	$\bar{1}$	−38	38

The function $R = \Sigma||F_0| - |F_c|| \Big/ \Sigma|F_0|$ for the above reflections (about 200 in number) gave a value 0·20. This agreement between the observed and calculated values could be regarded satisfactory.

Due to the difference in ionic radii of Cl^{+5} and Br^{+5} ions the latter being appreciably larger, the unit cell dimensions and actual atomic

co-ordinates of barium bromate are slightly different from those of barium chlorate monohydrate. However, comparing the structure of the two crystals we find that the atomic arrangements in the two crystals are similar, the bromate being obtained from that of the chlorate crystal by replacing the chlorines by the bromine atoms.

It is with great pleasure that the author thanks Prof. R. S. Krishnan for his kind interest and Dr. G. N. Ramachandran for guidance and help during these investigations.

SUMMARY

The crystal structure of barium bromate monohydrate has been determined and the atomic co-ordinates refined by differential synthesis and minimization methods as well as by Fourier methods. It is found that the atomic arrangement is closely similar to that in barium chlorate monohydrate.

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CHEMICAL EXAMINATION OF PLANT INSECTICIDES

Part VII. Further Study of Some Amorphous Fractions from the Root-Bark of *Tephrosia lanceolata* Grah.

By S. Rangaswami, F.A.Sc. and B. V. Rama Sastry

(From the Department of Pharmacy, Andhra University, Waltair)

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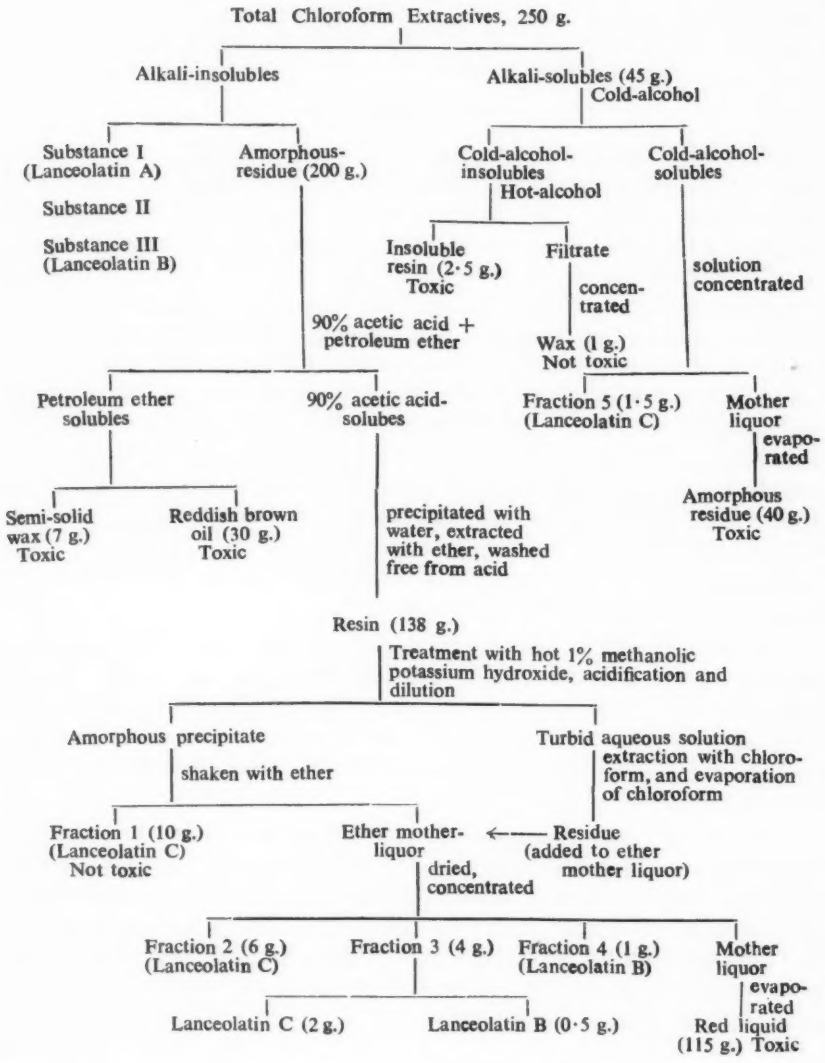
The powerful insecticidal property of rotenone led workers to believe at first that the insecticidal action of Derris root itself must be attributed to its rotenone content.[1] However, it was observed by later workers that extracts of Derris root poor in rotenone content or not having any rotenone at all could still be very active as insecticides.[2] It was further noticed that the amorphous fraction remaining after the removal of rotenone from various extracts exhibited high toxicity to fish and insects. A detailed study of these amorphous fractions resulted in the isolation of a number of crystalline substances closely related to rotenone like tephrosin, deguelin, toxicarol, malaccol and elliptone.[3] For the isolation of these, treatment of the extract with alkali was found to be essential, sometimes ordinary temperature being sufficient and sometimes higher temperatures being necessary. These substances were invariably obtained in an optically inactive form. It is now believed that they exist not as such in the resin but in the form of precursors or in some other unknown form of combination broken down by alkaline treatment yielding crystalline products.

In Part VI of this series[4] the isolation of three crystalline compounds (named then as Substances I, II and III) and some amorphous fractions from the chloroform and alcoholic extractives of the root-bark of *Tephrosia lanceolata* was described. As stated therein many of the amorphous fractions were toxic to fish. They have therefore been subjected to further examination now.

In view of the fact that Substances I and III have been met with in our laboratories not only in other parts of *T. lanceolata* but also in some other *Tephrosia* species it is now considered that it would be more convenient to give them more specific names. Consequently the names Lanceolatin A and Lanceolatin B are proposed for Substances I and III respectively of the previous communication; a name is not considered necessary for Substance II as it does not seem to occur widely.

The amorphous material remaining after the separation of Substances I (Lanceolatin A), II and III (Lanceolatin B) from the alkali-insolubles of the chloroform extractives was partitioned between 90% acetic acid and petroleum ether, according to the procedure described by Goodhue and

TABLE



Haller[5] in their study of the amorphous components of *Tephrosia virginiana* roots. The petroleum ether-soluble fraction could be separated into a waxy semi-solid and a thick reddish brown oil both of which exhibited toxicity towards fish. The 90% acetic acid-soluble fraction, on treatment with boiling methanolic potash, yielded two crystalline substances. One of them melted at 129°, had a composition corresponding to the formula $C_{24}H_{20}O_5$ and was non-toxic to fish. It is therefore considered to be a new substance and is designated as Lanceolatin C. The other crystalline substance proved to be identical with Lanceolatin B, *i.e.*, Substance III of the earlier communication. During this investigation it was observed that the substance could crystallise either in the hydrated form or in the anhydrous form depending upon the conditions employed, and that the hydrated form could lose its water slowly even on prolonged storage. The final mother liquor remaining after the removal of these substances yielded a reddish oil considerably toxic to fish.

The alkali-soluble part of the chloroform extractives of *Tephrosia lanceolata* was described in the earlier communication as amorphous. It has now been found that it could be divided into a cold alcohol-insoluble and a cold alcohol-soluble part. By treatment with boiling alcohol the former could be further divided into a more soluble waxy part which was non-toxic to fish and a less soluble resinous part which was toxic to fish. The cold alcohol-soluble part yielded on concentration a small crystalline fraction which proved to be identical with Lanceolatin C; the bulk of it, however, was amorphous and toxic to fish.

The course of the separations is shown in the above table.

Experimental

The separation of the total chloroform extractives of the root-bark of *Tephrosia lanceolata* into alkali-insolubles and alkali-solubles making use of 5% aqueous potassium hydroxide and the isolation of Substances I (renamed Lanceolatin A), II and III (renamed Lanceolatin B) from the former have been described in Part VI.

Alkali-insolubles.—The amorphous toxic residue recovered from the mother liquors after separation of Substance I (Lanceolatin A), Substance II and Substance III (Lanceolatin B) was taken up in 300 c.c. of glacial acetic acid and treated with 300 c.c. of petroleum ether, followed by 30 c.c. of water. The mixture was thoroughly shaken, and the layers were allowed to separate. The lower acetic acid layer was shaken with 3×50 c.c. of petroleum ether contained in a 2nd, 3rd and 4th separating funnel respectively. The petroleum ether solution in the first separator was washed with 3 further

quantities of 90% acetic acid, 50 c.c. each, and each of these washings passed in succession through the 2nd, 3rd and 4th separators containing petroleum ether as mentioned above. The four petroleum ether solutions and the four acetic acid solutions were separately united and treated further as described below.

The petroleum ether solution was washed with dilute alkali to remove acetic acid, then with very dilute hydrochloric acid to remove alkali and finally with water until free from acid, dried over anhydrous sodium sulphate, concentrated to 100 c.c. and left in the ice chest. A waxy semi-solid, reddish brown in colour, separated. The supernatent liquid was decanted off and the residue washed with petroleum ether by maceration and decantation of the supernatent liquid. The residual semi-solid could not be crystallised from any solvent. The solvent-free material (7 g., 0·18%) was toxic to fish (50 p.p.m. in 16 minutes; 100 p.p.m. in 10 minutes). Evaporation of the combined petroleum ether mother liquor and washings under vacuum left behind 30 g. (0·79%) of a thick reddish brown oil which was toxic to fish (20 p.p.m. in 42 minutes; 50 p.p.m. in 10 minutes; 200 p.p.m. in 5 minutes).

The 90% acetic acid-soluble fraction was recovered by dilution with water (1,000 c.c.) and extraction with ether (3 × 200 c.c.). The combined ether solution was extracted repeatedly with alkali until the acidity due to acetic acid was completely removed, then with 2% hydrochloric acid and finally with water till neutral. It was then dried over anhydrous sodium sulphate, filtered and concentrated to 200 c.c., the remaining ether being removed under suction.

The resulting neutral resin (138 g.; 2·8%) was dissolved in warm methyl alcohol (270 c.c.) and treated with 10% aqueous potassium hydroxide (30 c.c.). No solid separated. The solution was boiled under reflux for 15 minutes, cooled and left in the ice chest overnight. Still no solid separated. The alkali was neutralised with 1 : 1 hydrochloric acid and the solution diluted with water (500 c.c.). An amorphous solid settled down. The turbid supernatent liquid was decanted into another flask, and the solid was washed with water by grinding and decantation of the aqueous liquid. The amorphous solid was then shaken with 500 c.c. of ether whereby the whole of the substance went into solution but immediately a yellow crystalline substance (Fraction 1) was deposited in the form of irregular plates and prisms. The substance was filtered off and thoroughly washed with ether. The ethereal filtrate was treated further as described below.

The turbid aqueous supernatent liquid and washings mentioned above were extracted with chloroform; the chloroform solution was washed free

from acid, dried over anhydrous sodium sulphate, filtered and the solvent removed under reduced pressure. The residue was added to the ethereal filtrate mentioned at the end of the last para.

The ether mother liquor from Fraction 1 was dried over anhydrous sodium sulphate, filtered and concentrated to 200 c.c. On keeping in the ice chest for fifteen days a yellow solid (Fraction 2) was deposited. The mother liquor from Fraction 2 deposited two more fractions (Fractions 3 and 4) at intervals of 10 days. No further crystalline fraction was obtained from the mother liquor even after keeping in the ice chest for a month. The residue obtained by evaporation of the solvent under vacuum was a red liquid miscible with alcohol, acetone and benzene. It was highly toxic to fish (50 p.p.m. in 11 minutes; 20 p.p.m. in 20 minutes).

Alkali-solubles.—The semi-solid (45 g.) representing the alkali-soluble fraction of the chloroform extract (*see* Part VI) was treated with 200 c.c. of methylated spirit. Most of it went into solution but a small quantity of a wax-like solid was found to remain undissolved. It was filtered and the filtrate was concentrated to 125 c.c. and left in the ice chest for 10 days, whereupon a yellow coloured crystalline fraction was deposited (Fraction 5). It was filtered. No more crystalline material could be obtained from the filtrate by further concentration and leaving in the ice chest for one month. The red semi-solid residue (40 g.) obtained by evaporating the solvent under vacuum was toxic to fish (34 p.p.m. in 17 minutes; 86 p.p.m. in 10 minutes; 171 p.p.m. in 6 minutes).

The wax-like solid mentioned above was boiled with methylated spirit (100 c.c.). A dark resinous solid remained insoluble. The alcohol solution was decanted off and the insoluble residue treated with further quantities of boiling methylated spirit (3×50 c.c.) and the solution was decanted off each time. The combined warm alcohol solution was filtered, concentrated to 100 c.c. and kept in the ice chest. The wax that was deposited was filtered and dried. The residue obtained by complete evaporation of the filtrate was insignificant in amount and was not examined further. The wax (dry weight 1 g.) melted at 75 to 84° C.; it did not answer Durham test and was not toxic to fish. (The fish lived for 24 hours in a concentration of 67 p.p.m. Tests with higher concentrations could not be carried out as the wax separated out even though gelatin was added as a stabiliser). No crystalline material could be obtained by taking the hot alcohol-insoluble reddish-brown resin in any other solvent. The solid amounting to 2·5 g. was toxic to fish, 50 p.p.m. in 43 minutes. (The initial solution was prepared with acetone; the acetone concentration in the final aqueous solution was below 0·1%).

Fraction 1. (Yield, 10 g.).—After crystallisation from methanol-acetone thick hexagonal plates, pale orange in colour and melting at 125–27°. On further crystallisation first from acetone and then from ethyl acetate, m.p 129°. This is referred to as Lanceolatin C.

Fraction 2. (Yield, 6 g.).—After two crystallisations from methanol-acetone and ethyl acetate it melted at 129° and was identical with Lanceolatin C.

Fraction 3. (Yield, 4 g.).—This was fractionally crystallised from methanol. Lanceolatin C crystallised out as the first crop. On concentration of the mother liquor and keeping in the ice chest another substance separated out in the form of pale yellow needles. After further crystallisation from benzene it was found to be identical with the substance comprising Fraction 4.

Fraction 4. (Yield, 1 g.).—On crystallisation from ethyl acetate and then from methylated spirit almost colourless stout needles were obtained. Colour reactions same as described under Substance III in Part VI. The m.p. of the present sample after drying in vacuum at 100° for 2 hours (*viz.*, 148–49°) was undepressed by admixture with a similarly dried sample of Substance III described in Part VI and now called Lanceolatin B (Found on sample dried in vacuum: C, 78·18; H, 4·59; $C_{23}H_{14}O_4$ requires C, 77·96; H, 3·96%).

Fraction 5. (Yield, 1·5 g.)—Crystallised from methanol-acetone it melted at 126–27°. On recrystallisation from methanol-chloroform it was obtained as yellow plates, m.p. 129°. The substance was identical with Lanceolatin C (mixed m.p. and colour reactions).

Lanceolatin C.—It crystallised from ethyl acetate as layers of pale orange thick hexagonal plates melting at 129°. It was sparingly soluble in ethyl and methyl alcohols, moderately soluble in ether, soluble in warm benzene and carbon tetrachloride and freely soluble in acetone and chloroform. In chloroform solution it was optically inactive. It was insoluble in aqueous potassium hydroxide but soluble in alcoholic potassium hydroxide. With alcoholic ferric chloride it gave a red colour. It dissolved in concentrated sulphuric acid forming a yellow solution. It gave a red colour in the Liebermann-Burchard reaction and a pale yellow colour on reduction with magnesium and hydrochloric acid. It did not answer Durham test and Gross-Smith-Goodhue test. The substance was not toxic to fish even after 24 hours in a concentration of 167 p.p.m. (Acetone was used to prepare the solution. The acetone concentration in the final test solution was slightly below 0·1%; in this concentration the solvent has no adverse effect on the fish). Owing to the sparing solubility of the substance the

toxicity test could not be conducted with higher concentrations (Found: C, 73·96; H, 5·24; $C_{24}H_{20}O_5$ requires C, 74·23; H, 5·15%).

Summary

The results obtained by a more detailed study of some of the amorphous fractions described in the previous communication on the root bark of *Tephrosia lanceolata* are herein recorded. Treatment of the amorphous residues after separation of Substance I (renamed Lanceolatin A), Substance II and Substance III (renamed Lanceolatin B) with methanolic potassium hydroxide has enabled the isolation of another crystalline substance, now named Lanceolatin C and further quantities of Lanceolatin B. Lanceolatin C is biologically inactive (fish test). The alkali-soluble portion of the chloroform extract of the root bark was also found to contain a small amount of Lanceolatin C. Several other active and inactive amorphous fractions are also described.

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MANGANESE GARNETS FROM CHIPURUPALLE AREA, VIZAGAPATAM DISTRICT

By J. S. R. Krishna Rao

(*Geology Department, Andhra University, Waltair*)

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(Communicated by Prof. C. Mahadevan, F.A.SC.)

Introduction

The garnets form a well-defined group of minerals with respect to their essential chemistry, physical constants and geological environment. They are considered as mixtures of two or more garnet molecules in varying proportions. Fermor[1] (1909) reported from Vizagapatam District garnets intermediate in composition between spessartite and andradite and gave them the name " Spandites ". They were considered by him to be igneous in origin and associated with ' Kodurite '[2] series of Vizagapatam District. Middlemiss[6] (1914) drew attention to the close similarity of ' Spandites ' to spessartites of Central Provinces, and stressed the need for further work on the composition of spandites.

Garnets occurring in manganiferous deposits of Chipurupalle area were carefully separated; their physical, optical and chemical properties were determined, and chemical composition, compared with other manganese garnets.[5] Of the six garnets studied, four were taken from Kodurites, and the other two were taken from manganese ores.

Occurrence

Garnets occur as disseminated granular grains in manganese ores such as pyrolusite, psilomelane and wad. They also occur in para-gneisses (Khondalite series), hybrids (' Kodurites'), and intrusive granitic gneisses which constitute the rock formations of the area. Most of the garnets are red to blood-red and pink in colour while a few are brown and yellow. The blood-red and yellow coloured garnets occur in manganese ores and the red, pink and brown coloured garnets occur in Kodurites. They are vitreous to adamantine in lustre and range in specific gravity from 3·8 to 4·2. They are pitted in appearance showing high relief and are isotropic. They contain inclusions of quartz and magnetite. They show partial alteration to hydrated manganese oxides along the irregular cracks.

Chemical Analyses of Garnets

	A	B	C	D	G_1	G_2
SiO_2 ..	52·31	39·97	38·25	34·80	20·30	36·84
Al_2O_3 ..	14·00	20·00	7·00	13·00	14·87	11·78
Fe_2O_3 ..	18·54	20·54	33·24	28·42	14·14	11·20
FeO ..	1·46	1·46	5·16	8·48	2·80	2·20
MnO ..	9·89	5·66	4·23	3·50	33·03	25·45
CaO ..	1·00	5·80	11·64	0·80	15·00	11·80
MgO ..	2·00	6·00	1·24	0·20	0·65	0·52
H_2O + ..	0·20	0·15	0·10	0·19	0·12	0·12
H_2O − ..	0·08	0·06	0·04	0·07	0·02	0·04
	99·48	99·64	100·90	99·46	99·93	99·95
Specific gravity	3·8	3·9	4·2	4·2	4·0	4·1

Analyst: J. S. R. Krishna Rao

A—Blood-red in colour, Locality: Avagudem
B—Yellow in colour, Locality: Chokrapalem
} Occur in manganese ores.

C—Brown in colour, Locality: Chokrapalem
D—Red in colour, Locality Vedullavalasa
G_1 & G_2—Brown in colour, Locality: Garraju Chipurupalle
} Occur in Kodurites.

The above table shows that the constituents vary from one garnet to the other. MnO is the most varying constituent from 3·5% to as much as 32·03%. All the garnets show high content of iron; Calcium is comparatively more variable than magnesium.

Chemical Composition

The molecular formulæ for the above garnets were calculated, and can be expressed as follows:

A — $Sp_{48}\ Cal_{40}\ py_6\ Al_2\ An_2\ Gr.$

B — $Sp_{11}\ Cal_{50}\ py_{21}\ Al_2\ An_{14}\ Gr.$

C — $Sp_6\ Cal_{54}\ py_3\ Al_8\ An_{18}\ Gr_5.$

D — $Sp_{20}\ Cal_{60}\ py\ Al_{15}\ An\ Gr.$

G_1 and G_2 — $Sp_{53}\ py_2\ Al_5\ An_{38}\ Gr.$

These formulæ show wide variation in composition. There are all possible gradations from spessartites and calderites to andradites and almandites. These garnets are rich in manganese, and comparatively poor in calcium and magnesium. These are essentially similar in chemical composition to spessartites in that both are manganese rich.

ALTERATION

These garnets along with other manganese pyroxenes alter, giving rise to the formation of manganese ore bodies. The alteration may be brought about by meteoric waters highly charged with carbon dioxide leaving behind free silica, alumina, and iron oxide, as chert, kaolin, and lithomarge respectively.

ORIGIN

These garnets appear to have been formed from original impure manganiferous sediments. Variation in composition, association with para-gneisses and hybrids, similarity in composition with spessartites[3] of Madhya Pradesh (C.P.) and calderites[4] of Hazaribagh (Bihar) strongly suggest a metamorphic origin for these garnets.

SUMMARY

1. Manganese garnets of Vizagapatam District called by Fermor "Spandites" are metamorphic in origin and are mixtures of the garnet molecules—spessartite, calderite, almandite and andradite.

2. They are essentially similar to spessartites of Central Provinces in that they are formed due to the metamorphism of manganiferous sediments.

ACKNOWLEDGMENT

I am greatly indebted to Prof. C. Mahadevan, M.A., D.Sc., for the suggestion of the problem, guidance and the keen interest he has taken during the progress of the work.

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CHLORAMPHENICOL SERIES

Part I. Nitrophenyl Alkyl Sulphides, Sulphoxides and Sulphones

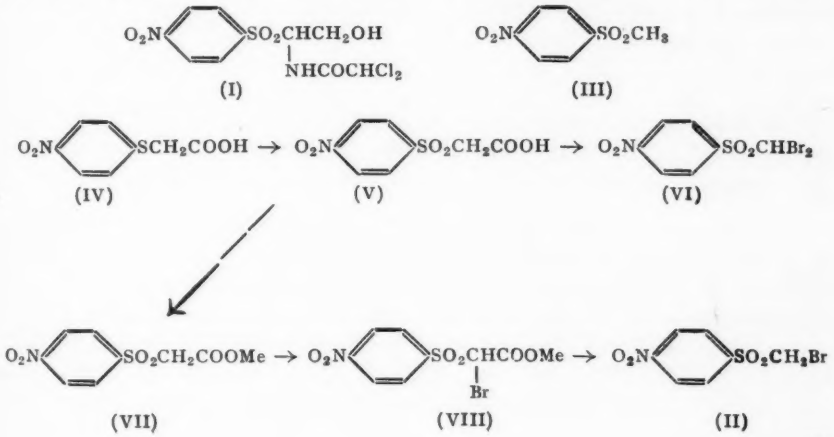
By A. V. Sunthankar, B. D. Tilak, F.A.Sc. and
K. Venkataraman, F.A.Sc.

(*Department of Chemical Technology, University of Bombay, Matunga, Bombay*)

Received May 2, 1953

In view of the high antibacterial activity of compounds containing the sulphone group, such as sulphanilamides and 4 : 4′-diaminodiphenyl sulphone, the synthesis of *p*-nitrophenyl α-dichloroacetamido-β-hydroxyethyl sulphone (I) was undertaken. Compound (I) contains all the structural features of chloramphenicol (Chloromycetin, Parke Davis & Co.) with the exception of the —CHOH— group, which has been replaced by the sulphone group in (I). While this work was in progress, highly active sulphide and sulphone analogues of chloramphenicol, in which the nitro group is replaced by thioalkyl and alkyl sulphonyl groups have been reported.[1]

The synthesis of (I) from *p*-nitrophenyl bromomethyl sulphone (II), by analogy with the synthesis of chloramphenicol from *p*-nitrophenacyl bromide, was first planned; but in contrast to the facile bromination of *p*-nitroacetophenone, the bromination of *p*-nitrophenyl methyl sulphone (III) could not be effected by any of the usual methods. An alternative synthesis of (II) from *p*-nitrophenyl carboxymethyl sulphone (V) was then

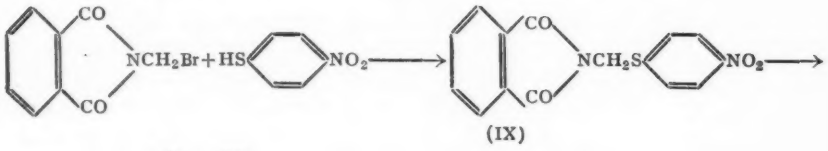


attempted, (V) being obtained by oxidation of *p*-nitrophenyl carboxymethyl sulphide (IV). However, bromination of (V) in acetic acid gave *p*-nitrophenyl dibromomethyl sulphone (VI) and not the desired monobromo acid or (II). The bromo compound (II) was finally synthesized by bromination of *p*-nitrophenyl carbomethoxymethyl sulphone (VII) to *p*-nitrophenyl bromocarbomethoxymethyl sulphone (VIII) and treatment of the latter with aqueous sodium hydroxide.

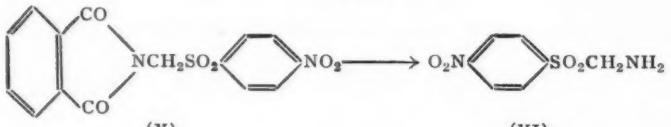
The bromo derivative (VIII) was unaffected by treatment with hexamine and gave phenyl methyl sulphone on heating at 160° with liquor ammonia under pressure.

Attempts to react (II) with reagents which should lead to the synthesis of *p*-nitrophenyl aminomethyl sulphone (XI) (or its hydrochloride) were unsuccessful. Among the reagents which were employed in these attempts were hexamine, sodamide, liquor ammonia and potassium phthalimide.

On the basis of the known synthesis of chloramphenicol from *p*-nitrophenyl acetamidomethyl ketone, the following alternative route to (I) was then investigated:



(IX)



(X) (XI)

Hydrolysis of *p*-nitrophenyl phthalimidomethyl sulphide (IX) and *p*-nitrophenyl phthalimidomethyl sulphone (X), however, proved unsuccessful. Attempts to hydroxymethylate (X) were also unsuccessful.

These results indicate that the methyl group attached to the sulphone group in *p*-nitrophenyl methyl sulphone (III) is not active, unlike the methyl group in *p*-nitroacetophenone. Similarly the bromine atom in (II) is not reactive, unlike the bromine atom in *p*-nitrophenacyl bromide. The deactivating influence of the sulphone group in contrast with the activating influence of the carbonyl has also been reported in the literature.[2] Alternative routes to (I) starting from benzene sulphenyl chloride and nitroalkanes, are under investigation.

In view of the reported[3] activity of *p*-nitrophenyl ω-hydroxyethyl sulphide, sulphoxide and sulphone, the following compounds have been prepared: *p*-Nitrophenyl ω-hydroxyethyl sulphide, *p*-nitrophenyl ω-hydroxyethyl sulphoxide, *p*-nitrophenyl ω-hydroxyethyl sulphone, 2:6-diiodo-4-nitrophenyl carboxymethyl sulphide, *p*-nitrophenyl carboxymethyl sulphoxide, *p*-nitrophenyl carboxyamidomethyl sulphide, *p*-aminophenyl ω-hydroxyethyl sulphide and *p*-nitrophenyl 2:3-dihydroxypropyl sulphide. The synthesis of these compounds was briefly reported earlier[4] and the present paper gives experimental details. Prof. B. V. Bhide and Mr. P. Y. Dighe have informed us that some of the compounds are highly active bacteriostatic agents, especially against the dysentery organisms of the Shigella group.[3]

Experimental

p-*Nitrophenyl carboxymethyl sulphone* (*V*)

p-Nitrophenyl carboxymethyl sulphide[5] (2 g.), hydrogen peroxide (5 c.c., 36%) and glacial acetic acid (10 c.c.) were heated on a water-bath at 80° for 10 hrs. After removal of acetic acid under reduced pressure, a dark brown solid (1·8 g.) was obtained. After three crystallizations from aqueous alcohol, it gave small white needles, m.p. 167° (Found: C, 39·2; H, 2·7; N, 5·8. $C_8H_7NO_6S$ requires C, 39·2; H, 2·8; N, 5·7%).

p-*Nitrophenyl dibromomethyl sulphone* (*VI*)

The foregoing sulphone (V) (1·3 g.) was dissolved in glacial acetic acid (10 c.c.) and bromine (0·5 c.c.) in glacial acetic acid (10 c.c.) was gradually added. The solution was then refluxed on an oil-bath at 140° for 4 hrs. At the end of the reaction, the colour of the solution was changed to greenish yellow. Acetic acid was then removed under reduced pressure and water (10 c.c.) was added to the reaction mixture when a white precipitate immediately separated (0·8 g.). It was filtered and washed with water. It gave pale yellow curved needles from benzene-*n*-hexane mixture, m.p. 170° (Found: C, 23·7; H, 1·4; Br, 43·8. $C_7H_5Br_2NO_4S$ requires C, 23·7; H, 1·4; Br, 44·5%).

p-*Nitrophenyl carbomethoxymethyl sulphone* (*VII*)

The sulphone (V) (1·2 g.), dimethyl sulphate (0·6 g.), sodium bicarbonate (0·75 g.) and acetone (50 c.c.) were refluxed for 10 hrs. After removal of acetone, the mixture was diluted with water. The product (1·5 g.), m.p. 110–15°, after three crystallizations from benzene-*n*-hexane mixture, gave small white needles, m.p. 125–26° (Found: C, 41·5; H, 3·4. $C_9H_9NO_6S$ requires C, 41·7; H, 3·5%).

p-*Nitrophenyl bromocarbomethoxymethyl sulphone* (*VIII*)

The ester (VII) (2·5 g.) was dissolved in glacial acetic acid (20 c.c.) and bromine (3 g.) in glacial acetic acid (20 c.c.) was gradually added. The solution was then refluxed for 4 hrs. at 140°. The colour of the solution gradually turned to greenish yellow. Acetic acid was removed under reduced pressure and the dark brown liquid was diluted with cold water. The product which separated was crystallized from aqueous alcohol, when it gave small white needles (2 g.), m.p. 118–20°; raised to 130–31° by further recrystallization from benzene-*n*-hexane (Found: C, 31·5; H, 2·4. $C_9H_8BrNO_6S$ requires C, 31·9; H, 2·4%).

p-*Nitrophenyl bromomethyl sulphone* (*II*)

A mixture of the sulphone (VIII) (0·4 g.) and aqueous sodium hydroxide (10%) (5 c.c.) was shaken vigorously. The colour of the mixture first became orange and slowly changed to pale yellow and finally white. The crystalline structure of the sulphone (VIII) rapidly changed and small needles were obtained. The mixture was kept at room temperature for 2 hours and filtered. The residue was washed free from alkali and the crystalline product (0·26 g.), m.p. 134–42°, was recrystallized thrice from alcohol when it gave long white needles, m.p. 163–64° (Found: C, 30·1; H, 2·4; N, 5·2. $C_7H_6BrNO_4S$ requires C, 30·0; H, 2·1; N, 5·0%).

p-*Nitrophenyl phthalimidomethyl sulphide* (*IX*)

Sodium (1 g.) was dissolved in absolute alcohol (30 c.c.), *p*-nitrothiophenol (6·9 g.) was added and the mixture was refluxed for 10–15 mins. Bromomethyl phthalimide[6] (10·7 g.) was added and the mixture was refluxed further for 4 hours. At the end of the reaction the colour of the solution changed from dark red to yellow and a yellow precipitate was obtained. The mixture was concentrated, cooled and the yellow crystalline compound (12 g.), m.p. 175°, which separated was collected. It was purified by three crystallizations from acetic acid when (IX) gave m.p. 180–81° (Found: C, 57·7; H, 3·3; N, 8·9. $C_{15}H_{10}N_2O_4S$ requires C, 57·3; H, 3·1; N, 8·8%).

p-*Nitrophenyl phthalimidomethyl sulphone* (*X*)

The foregoing sulphide (X) (1 g.), hydrogen peroxide (112 vols.) (10 c.c.) and glacial acetic acid (20 c.c.) were heated on a water-bath at 70–80° for 12 hrs. The yellow solid gradually changed to white. Acetic acid was then removed under reduced pressure and the white product (1 g.) crystallized thrice from dioxane when it gave white plates, m.p. 265° (dec.) (Found: C, 52·2; H, 3·1; N, 8·2. $C_{15}H_{10}N_2O_6S$ requires C, 52·0; H, 2·9; N, 8·2%).

p-*Nitrophenyl ω-hydroxyethyl sulphide*

An alcoholic solution of *p*-nitrothiophenol (9·0 g. in 20 c.c.) was added to sodium ethoxide prepared by dissolving sodium (1·36 g.) in absolute alcohol (25 c.c.). The mixture was refluxed for 15 mins. and then ethylene monochlorhydrin (7 g.) was added, when the red colour of the thiophenolate solution immediately changed to yellow. The mixture was refluxed for 4 hrs. and alcohol was then removed by distillation. The mixture was diluted with water and extracted with ether. The ether extract was washed and dried (Na_2SO_4) and ether removed. The dark yellow liquid (10 g.), which was obtained as residue, soon solidified on cooling. Crystallization of the product from alcohol gave yellow plates, m.p. 60°, of the sulphide. Bennett and Berry,[7] who have prepared the sulphide from *p*-nitrochlorobenzene without isolation of the intermediate thiol give m.p. 62° (Found: C, 48·5; H, 4·8. Calc. for $C_8H_9NO_3S$: C, 48·2; H, 4·5%).

The hydroxyethyl sulphide (200 mg.) and phenyl isocyanate (110 mg.) were heated on a water-bath under anhydrous conditions for 3 hrs. The reaction product, after three crystallizations from benzene *n*-hexane, gave lemon yellow needles, m.p. 122° of the urethane (Found: N, 8·8. $C_{15}H_{14}N_2O_4S$ requires N, 9·0%).

p-*Nitrophenyl ω-acetoxyethyl sulphide*

A mixture of the foregoing sulphide (3 g.), acetic anhydride (10 c.c.) and a drop of pyridine was refluxed for 6 hrs. The excess of acetic anhydride was then removed under reduced pressure and the dark oil obtained was poured into crushed ice. The dark-coloured precipitate (3·1 g.) was filtered, washed and crystallized from aqueous alcohol, when it gave colourless needles, m.p. 44° (Found: N, 6·1. $C_{10}H_{11}NO_4S$ requires N, 5·8%).

p-*Nitrophenyl ω-hydroxyethyl sulphoxide*

A mixture of the above acetoxy sulphide (1·1 g.), hydrogen peroxide (112 vols.) (0·8 c.c.) and glacial acetic acid (5 c.c.) was heated in a boiling water-bath for 1 hour. It was poured into a saturated solution of sodium chloride. The white precipitate (1 g.) of the sulphoxide which separated was collected, dried and crystallized from alcohol when it gave lustrous colourless flakes, m.p. 125–26° (Found: C, 44·2; H, 4·2. $C_8H_9NO_4S$ requires C, 44·6; H, 4·2%). The oxidation could also be effected by means of 50 vols. hydrogen peroxide. The elementary analysis of the product indicated that the acetyl group in *p*-nitrophenyl ω-acetoxyethyl sulphide was cleaved during the oxidation.

The above sulphoxide was also obtained directly from *p*-nitrophenyl ω-hydroxyethyl sulphide by oxidation with hydrogen peroxide (100 vols.) in one experiment, but attempts to repeat the preparation were unsuccessful. The sulphoxide is, however, consistently obtained through the acetoxy sulphide as described above.

p-*Nitrophenyl ω-hydroxyethyl sulphone*

p-Nitrophenyl ω-hydroxyethyl sulphide (2 g.), hydrogen peroxide (120 vols.) (20 c.c.) and acetic acid (10 c.c.) were heated on a water-bath at 70–80° for 10 hrs. Removal of acetic acid under reduced pressure, gave a white product which on crystallization from aqueous alcohol, gave small colourless needles (1·56 g.), m.p. 124–25° of the sulphone (Found: C, 42·0; H, 4·0. $C_8H_9NO_6S$ requires C, 41·6; H, 4·0%). The sulphone was also obtained when 50 vol. hydrogen peroxide was used. The mixed m.p. of the above sulphoxide and the sulphone was 100–05°. *p*-Nitrobenzoyl chloride (0·7 g.) (freshly prepared from *p*-nitrobenzoic acid), the above sulphone (0·5 g.) and dry pyridine (0·5 c.c.) were heated on an oil-bath at 130–40° for 2 hrs. The liquid was then poured into ice. The white precipitate obtained was separated by filtration, washed with sodium bicarbonate and then with water. The *p*-nitrobenzoate of the sulphone gave colourless needles from benzene-*n*-hexane mixture, m.p. 164–65° (Found: C, 47·7; H, 3·4. $C_{15}H_{12}N_2O_8S$ requires C, 47·4; H, 3·1%).

p-*Aminophenyl ω-hydroxyethyl sulphide*

A mixture of *p*-nitrophenyl ω-hydroxyethyl sulphide (3 g.) and absolute alcohol (20 c.c.) and Raney nickel (0·5 g.) was shaken in a Parr hydrogenator with hydrogen at 42 lb./sq. inch for 6 hrs. The mixture was filtered and alcohol removed by distillation when a dark brown liquid (2·5 g.) was obtained. It gave a pale coloured liquid after four distillations and was finally collected at 190° (bath temp.)/15 mm. Morgan and Hamilton[8] quote m.p. 43–44° and b.p. 232–35°/38 mm. (Found: C, 56·1; H, 6·5. Calc. for $C_8H_{11}NOS$: C, 56·8; H, 6·5%).

p-*Nitrophenyl carboxyamidomethyl sulphide*

p-Nitrophenyl carboxymethyl sulphide (IV) (2 g.) and thionyl chloride (10 c.c.) were heated on a water-bath for 2 hrs. After removal of thionyl chloride, the dark liquid obtained was slowly added to liquor ammonia kept in an ice-bath. Yellow precipitate, m.p. 146–48°, immediately separated. It gave long lemon yellow needles, m.p. 159–60°, of the amide from aqueous alcohol (literature,[9] m.p. 159–60°) (Found: N, 13·1. Calc. for $C_8H_8N_2O_3S$: N, 13·2%).

2: 6-*Diiodo-4-nitrophenyl carboxymethyl sulphide*

p-Nitrophenyl carboxymethyl sulphide (IV) (1·24 g.) was heated on a water-bath at 70–80° with glacial acetic acid (10 c.c.). A solution of iodine monochloride (0·6 c.c.) in glacial acetic acid (4 c.c.) was slowly added under stirring, and the mixture was heated at 70–80° for 20 minutes under stirring. The brown yellow precipitate which separated was collected, washed with water and then with acetone. It crystallized in brownish yellow plates (0·55 g.), m.p. 112° (decomp.) from acetic acid (Found: N, 3·0. $C_8H_5I_2NO_4S$ requires N, 3·0%). The iodo derivative decomposes on keeping.

p-*Nitrophenyl carboxymethyl sulphoxide*

p-Nitrophenyl carboxymethyl sulphide (IV) (2 g.), glacial acetic acid (10 c.c.) and hydrogen peroxide (4 c.c.) were heated on a water-bath at 70–80° for 4 hrs. After removal of acetic acid under reduced pressure a dark brown liquid was obtained (1·8 g.) which solidified at room temperature. The product crystallized from aqueous alcohol in pale yellow needles, m.p. 140–41° (Found: C, 41·9; H, 3·4. $C_8H_7NO_5S$ requires C, 41·9; H, 3·1%).

p-*Nitrophenyl* 2: 3-*dihydroxypropyl sulphide*

p-Nitrothiophenol (5 g.) was added to a solution of sodium (0·75 g.) in absolute alcohol (30 c.c.). The solution was refluxed for 15 mins. and a solution of glycerine α-monochlorhydrin (4 g.) in absolute alcohol (10 c.c.) was slowly added. The mixture was refluxed on a water-bath for 4 hrs., the solvent removed by distillation and the mixture, after dilution with water, was extracted with ether. Removal of ether gave a dark yellow liquid (8·2 g.) which solidified after cooling. The sulphide crystallized from aqueous alcohol in yellow needles, m.p. 93° (Found: C, 47·2; H, 4·6; N, 6·2. $C_9H_{11}NO_4S$ requires C, 47·2; H, 4·8; N, 6·1%).

Summary

p-Nitrophenyl bromomethyl sulphone (II) and *p*-nitrophenyl phthalimidomethyl sulphone (X) were prepared with the view to synthesize the sulphone analogue (I) of chloramphenicol. In contrast with the synthesis of chloramphenicol from analogous phenacyl derivatives, (II) and (X) could not be converted to (I) on account of the deactivating influence of the sulphone group in aryl methyl sulphones.

In view of the activity of *p*-nitrophenyl ω-hydroxyethyl sulphide, sulphoxide and sulphone, several *p*-nitrophenyl alkyl sulphides, sulphoxides and sulphones and other related compounds were prepared.

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CHROMONES

Part IV. Nitration of 5-Hydroxychromone Derivatives and Their Methyl Ethers

By R. M. Naik, A. M. Mehta, V. M. Thakor, G. V. Jadhav and R. C. Shah, F.A.Sc.

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In continuation of the work earlier reported on nitration of chromones,[1] nitration of 5-hydroxy-2-methylchromone, 5-hydroxy-flavone and their methyl ethers has now been investigated and the constitution of the products established.

Nitration of 5-hydroxy-2-methylchromone (I, R = H, R_1 = Me) with nitric acid (d. 1·42) in acetic acid or concentrated sulphuric acid at 0° gave a mononitro derivative, m.p. 218°. On alkaline hydrolysis it furnished 2:6-dihydroxy-3-nitroacetophenone (II). As is obvious, the constitution of the mononitro derivative could not be determined by alkaline degradation as both the 6-nitro (V, R = H, R_1 = Me) and 8-nitro (III, R = H, R_1 = Me) chromones would yield a 4-nitroresorcinol derivative.

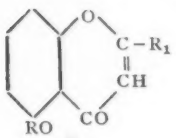
5-Hydroxy-2-methyl-6-nitrochromone (m.p. 161°) has been recently synthesised by Naik and Thakor,[2] by Kostanecki-Robinson acetylation of 2:6-dihydroxy-3-nitroacetophenone (II). As stated by them, due to its doubly chelated structure, this compound (IV) could be expected to give a 6-nitrochromone derivative (V, R = H; R_1 = Me). Hence, the mononitro product, m.p. 218°, must be 5-hydroxy-2-methyl-8-nitrochromone (III, R = H, R_1 = Me).

It is interesting to note that while 5-hydroxy-2-methyl-6-nitrochromone (V, R = H, R_1 = Me), like simple 5-hydroxy-2-methyl-chromone,[3] on alkaline degradation underwent ketone splitting to give 4-nitroresorcinol presumably through the corresponding γ-resorcylic acid derivative,[2] in the present case the 8-nitro isomer (III, R = H, R_1 = Me) on hydrolysis furnished 2:6-dihydroxy-3-nitroacetophenone (II).

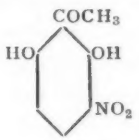
When the nitration was carried out at 100° with nitric acid (d. 1·42) in acetic acid, a dinitro derivative, m.p. 204–05° was obtained. The same product was also obtained on nitration of 5-hydroxy-2-methyl-6-nitrochromone (V, R = H, R_1 = Me) and 5-hydroxy-2-methyl-8-nitrochromone

(III, R = H, R_1 = Me) and on alkaline hydrolysis it furnished 2:6-dihydroxy-3:5-dinitroacetophenone (VII). The product was, therefore, 5-hydroxy-2-methyl-6:8-dinitrochromone (VI, R = H, R_1 = Me).

The hitherto unknown 5-methoxy-2-methylchromone (I, R = R_1 = Me) was prepared by the usual method. On nitration with nitric acid (d. 1·42) and concentrated sulphuric acid at 0°, it gave a mononitro derivative, m.p. 215°. However, 5-hydroxy-2-methyl-8-nitrochromone could not be methylated and the usual methods of demethylation failed in case of this methoxy-nitro derivative. With boiling sodium hydroxide solution it furnished 2-acetyl-4-nitroresorcinol, demethylation and degradation occurring simultaneously. On keeping it with aqueous sodium hydroxide at room temperature (30°) however, 5-hydroxy-2-methyl-8-nitrochromone (III, R = H, R_1 = Me) was obtained. Demethylation also occurred with boiling alcoholic potassium hydroxide. Hence the product was 5-methoxy-2-methyl-8-nitrochromone (III, R = R_1 = Me). Thus, during alkaline hydrolysis, presumably demethylation precedes degradation.



(I)



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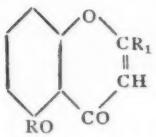

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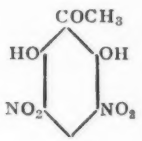

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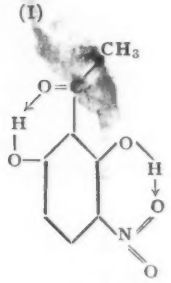

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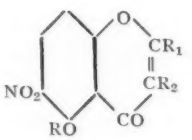

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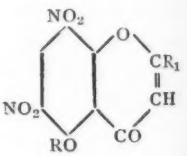

(VI)

Further nitration of 5-methoxy-2-methyl-8-nitrochromone, with nitric acid (d. 1·42) and sulphuric acid at room temperature (30°) furnished 5-hydroxy-2-methyl-6:8-dinitrochromone, demethylation occurring simultaneously. This further indicates the labile nature of the methoxy group in these nitrochromones.

5-Hydroxyflavone (I, R = H, R_1 = Ph) when treated with nitric acid (d. 1·42) in sulphuric acid at 0° afforded a mononitro derivative, m.p.

225–26°, which on alkaline hydrolysis gave 2: 6-dihydroxy-3-nitroacetophenone (II). It has been assigned the constitution, 5-hydroxy-8-nitroflavone (III, R = H, R_1 = Ph), as it was different from 5-hydroxy-6-nitroflavone (V, R = H, R_1 = Ph), m.p. 209°, obtained by Naik and Thakor[2] on Kostanecki-Robinson benzoylation of 2: 6-dihydroxy-3-nitroacetophenone (II) and subsequent hydrolysis of 5-hydroxy-3-benzoyl-6-nitroflavone obtained.

Nitration of the flavone (I, R = H, R_1 = Ph) at 100° afforded a dinitro derivative, 5-hydroxy-6: 8-dinitroflavone, m.p. 253–54° (V, R = H, R_1 = Ph). It was also obtained on further nitration of 5-hydroxy-6-nitroflavone (V, R = H, R_1 = Ph) and 5-hydroxy-8-nitroflavone (III, R = H, R_1 = Ph) and on hydrolysis gave 2: 6-dihydroxy-3: 5-dinitroacetophenone (VII).

6-Methoxyflavone (I, R = Me, R_1 = Ph) on nitration with nitric acid (d. 1·42) and sulphuric acid at 0° afforded a dinitro derivative. On hydrolysis with aqueous sodium hydroxide, 2: 6-dihydroxy-3-nitroacetophenone (II) was obtained, indicating only one nitro group in the benzene ring. Attempt to isolate any mononitrobenzoic acid, which may be formed as one of the products of hydrolysis, if the other nitro group is in the phenyl ring, proved futile. It could not be demethylated under the usual conditions, adopted in previous cases. The constitution of this compound thus could not be established. However, the nitro group in the benzene ring may be considered to be in 8-position rather than 6- from analogy with 5-methoxy-2-methylchromone. Tentatively the structure has been assigned as 5-methoxy-8: (?)-dinitroflavone.

Thus in 5-hydroxy-chromones, as would be expected, positions '6' and '8' are reactive. The nitration first takes place in the 8-position. It may be noted that on Fries rearrangement of 5-acetoxychromone derivatives the migration occurs to the 6-position.[4] Analogous behaviour has been observed in the coumarin series. Thus while Fries transformation of 5-acyloxycoumarins furnishes 6-acyl derivatives,[5] nitration leads to 8-nitrocoumarins.[6]

Experimental

Nitration of 5-Hydroxy-2-methylchromone (I, R = H, R_1 = Me) at 0°: 5-Hydroxy-2-methyl-8-nitrochromone (III, R = H, R_1 = Me)

5-Hydroxy-2-methylchromone,[7] m.p. 92° (1·0 g.) in acetic acid (10·0 c.c.) was treated with nitric acid (d. 1·42; 5·0 c.c.) at 0° and the mixture kept at that temperature for 2 hours. On dilution a brownish yellow precipitate was obtained and was crystallised from acetic acid in almost colourless plates,

m.p. 218° (Found: N, 6·5. $C_{10}H_7O_5N$ requires N, 6·3%). *5-Hydroxy-2-methyl-8-nitrochromone* (*III*, $R = H$, $R_1 = Me$) is sparingly soluble in alcohol and difficultly in benzene and ether. It gives dark red coloration with alcoholic ferric chloride. It is sparingly soluble in sodium hydroxide, insoluble yellow sodium salt separating out. *Acetyl* derivative separated as colourless needles from alcohol, m.p. 196–97° (Found: N, 5·5. $C_{12}H_9O_6N$ requires N, 5·3%).

The same mononitro compound was obtained when the nitration was carried out with nitric acid (d. 1·42; 5·0 c.c.) in concentrated sulphuric acid (10 c.c.) at 0°.

Attempts to methylate the compound with sodium hydroxide-dimethyl sulphate or methyl iodide-potassium carbonate (acetone) met with failures; similar also was the result when its sodium salt and dimethyl sulphate were refluxed in toluene or nitrobenzene.

Hydrolysis of 5-Hydroxy-2-methyl-8-nitrochromone (*III*, $R = H$, $R_1 = CH_3$): 2: 6-*Dihydroxy-3-nitroacetophenone* (*II*)

5-Hydroxy-2-methyl-8-nitrochromone (1·0 g.) was boiled with sodium hydroxide solution (6%; 25 c.c.) for 2 hours, cooled and acidified. The brown solid obtained on standing was collected and crystallised from dilute alcohol (50%) in yellow needles, m.p. 119°. Mixed melting point with an authentic specimen of 2: 6-dihydroxy-3-nitroacetophenone (II)[8] was not lowered.

Nitration of 5-Hydroxy-2-methylchromone (*I*, $R = H$, $R_1 = Me$) *at* 100°: 5-*Hydroxy-2-methyl*-6: 8-*dinitrochromone* (*VI*, $R = H$, $R_1 = Me$)

A mixture of 5-hydroxy-2-methylchromone (0·5 g.), acetic acid (10·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.) was heated on a steam-bath for half an hour and cooled. The yellow solid obtained on dilution was crystallised from acetic acid, yellow needles, m.p. 204–05° (Found: N, 10·3. $C_{10}H_6O_7N_2$ requires N, 10·5%). It is sparingly soluble in benzene and alcohol. It gives red coloration with alcoholic ferric chloride and is insoluble in alkali, the insoluble sodium salt separating out. *Acetyl* derivative was obtained in needles from alcohol, m.p. 155° (Found: N, 9·3. $C_{12}H_7O_8N_2$ requires N, 9·1%). Attempts at methylation of the product proved fruitless.

5-Hydroxy-2-methyl-6: 8-*dinitrochromone* (*VI*, $R = H$, $R_1 = Me$) was also obtained on nitration of 5-hydroxy-2-methyl-6-nitrochromone[2] (V, R = H, R_1 = Me) (0·5 g.) in acetic acid (10·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.) or 5-hydroxy-2-methyl-8-nitrochromone (III, R = H, R_1 = Me) (0·5 g.) in

acetic acid (10·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.) on a steam-bath for half an hour.

The above dinitrochromone (VI, R = H, R_1 = Me) (1·0 g.) on hydrolysis with boiling sodium hydroxide solution (2 N; 20 c.c.) for 4 hours furnished 2: 6-dihydroxy-3: 5-dinitroacetophenone[8] (VII), crystallised from dilute alcohol, m.p. and mixed m.p. 104°.

2: 6-*Dihydroxy*-3: 5-*dinitroacetophenone* (*VII*)

It was prepared by nitration of 2-acetylresorcinol by slightly modifying the method of Naik and Jadhav.[9]

Nitric acid (1·42 d.; 10·0 c.c.) was added dropwise with stirring to a solution of 2-acetylresorcinol (2·0 g.) in glacial acetic acid (20·0 c.c.) cooled to 5°. It was then kept at that temperature for 2 hours with occasional shaking. Steam was passed to remove any mononitro derivative. The residual liquid on cooling gave yellow crystals of 2: 6-dihydroxy-3: 5-dinitroacetophenone (VII). The mother-liquor on ether extraction gave a further quantity of the same. It was crystallised from boiling water in shining yellow needles, m.p. 104–05° (1·4 g.).

5-*Methoxy*-2-*methylchromone* (*I*, $R = R_1 = Me$)

5-Hydroxy-2-methylchromone (1·0 g.), dry potassium carbonate (5·0 g.), methyl iodide (4·0 c.c.) and dry acetone (50 c.c.) were refluxed on a warm water-bath for 24 hours. More methyl iodide (4·0 c.c.) was added and the mixture refluxed for further 24 hours. After filtering off the solid, acetone was removed and the mixture diluted with water. The oil that separated was washed with dilute sodium hydroxide solution and taken up in ether. On removing ether after drying, an oil was obtained which solidified on keeping in a desiccator under vacuum for 24 hours. It was crystallised from alcohol (95%) in colourless cubes, m.p. 102–03° (Found: C, 69·0; H, 5·3. $C_{11}H_{10}O_3$ requires C, 69·4; H, 5·2%). It does not give any coloration with alcoholic ferric chloride solution.

Nitration of 5-*Methoxy*-2-*methylchromone* (*I*, $R = R_1 = Me$) *at* 0°: 5-*Methoxy*-2-*methyl*-8-*nitrochromone* (*III*, $R = R_1 = Me$)

5-Methoxy-2-methylchromone (1·0 g.) was cooled externally to 0°, and a cooled mixture of concentrated sulphuric acid (5·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.) was added gradually with stirring. The mixture was left at 0° for one and half hours, poured into crushed ice, and the nitro compound that separated was collected, washed and crystallised from acetic acid in soft pale yellow plates, m.p. 215° (Found: N, 6·2. $C_{11}H_9O_5N$

requires N, 6·0%). Mixed m.p. with 5-hydroxy-2-methyl-8-nitrochromone was considerably depressed. It does not give any coloration with alcoholic ferric chloride solution. It gives no coloration with alkali, but turns yellow on keeping with it. Attempts to further nitrate the chromone (III, $R = R_1 = Me$) with nitric acid (d. 1·42) in acetic acid at 0°, 30° or 100° met with failures.

The nitrochromone (0·5 g.) was boiled with sodium hydroxide solution (10%; 10 c.c.) on a wire-gauze for about an hour when the whole of it went into solution. It was cooled and acidified and the product crystallised from alcohol (95%) in pale yellow needles, m.p. and mixed m.p. with 2:6-dihydroxy-3-nitroacetophenone (II), 119°.

Attempts at demethylating the nitrochromone with hydriodic acid in acetic anhydride or anhydrous aluminium chloride in nitrobenzene did not furnish any definite product. However, demethylation could be effected with aqueous or alcoholic alkali. The nitrochromone (0·5 g.) was refluxed with alcoholic potassium hydroxide on a warm water-bath for half an hour. Alcohol was removed and the yellow salt that remained was acidified and crystallised from acetic acid when 5-hydroxy-2-methyl-8-nitrochromone (III, $R = H$, $R_1 = Me$), m.p. and mixed m.p. 218°, was obtained. The same product was also obtained along with some 2:6-dihydroxy-3-nitroacetophenone when the nitrochromone (0·2 g.) was kept with sodium hydroxide solution (10%; 20 c.c.) at room temperature for 72 hours.

Nitration of 5-*Methoxy*-2-*methyl*-8-*nitrochromone* (*III*, $R = R_1 = Me$) *at* 28–30°: 5-*Hydroxy*-2-*methyl*-6:8-*dinitrochromone* (*VI*, $R = H$, $R_1 = Me$)

The nitrochromone (III, $R = R_1 = Me$) (0·5 g.) at 0° (external) was treated with a cooled mixture of concentrated sulphuric acid (5·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.). It was kept at room temperature (28–30°) for 20 hours and then poured into crushed ice. The yellow solid obtained was crystallised from acetic acid, and was identified as 5-hydroxy-2-methyl-6:8-dinitrochromone (VI, $R = H$, $R_1 = Me$), m.p. and mixed m.p. 204–05°.

5-*Hydroxyflavone* (*I*, $R = H$, $R_1 = Ph$)

It was prepared by the general method given by Virkar.[10]

2:6-Dibenzoyloxyacetophenone,[11] m.p. 105° (7·0 g.), was added to pulverised sodium (0·46 g.) in dry toluene (30 c.c.) and the mixture was heated at 130° for 8 hours. The separated sodium salt was collected and washed thoroughly with benzene. It was acidified with dilute acetic acid. 5-Hydroxy-3-benzoylflavone obtained was crystallised from glacial acetic

acid in yellow shining needles, m.p. 175°. Baker[11] had used anhydrous potassium carbonate and gives m.p. 177°; Sugasawa[12] gives m.p. 173–74°.

The debenzoylation could best be effected according to the method of Rajagopalan, Rao and Seshadri.[13] The above 3-benzoylflavone was gently refluxed with aqueous alcoholic sodium carbonate (5·0%; 200 c.c.) for 2 hours. The alcohol was removed under reduced pressure, the residue acidified and the brown solid crystallised from alcohol in pale yellow needles, m.p. 157° (2·0 g.). Sugasawa[12] gives m.p. 156–57°.

Nitration of 5-*Hydroxyflavone* (*I*, $R = H$, $R_1 = Ph$) *at* 0°: 5-*Hydroxy*-8-*nitroflavone* (*III*, $R = H$, $R_1 = Ph$)

5-Hydroxyflavone (0·5 g.) was treated with a mixture of sulphuric acid (5·0 c.c.) and nitric acid (d. 1·42; 5·0 c.c.) at 0° and left at that temperature for an hour. After working up as usual, the *nitroflavone* obtained was crystallised from acetic acid as fine crystals, which shrank at 200 and m.p. 225° (Found: N, 4·8. $C_{15}H_9O_5N$ requires N, 4·9%). Mixed melting point with 5-hydroxy-6-nitroflavone (m.p. 209°) was considerably depressed. It gives red coloration with alcoholic ferric chloride. It dissolves in sodium hydroxide on warming giving a yellow solution. It is sparingly soluble in hot alcohol and insoluble in ether and benzene. All attempts at its methylation were unsuccessful. *Acetyl* derivative, crystallised from alcohol, m.p. 239° (Found: N, 4·5. $C_{17}H_{11}O_6N$ requires N, 4·3%).

It was hydrolysed with sodium hydroxide solution (2 N) as usual when 2: 6-dihydroxy-3-nitroacetophenone (II), m.p. 119°, was obtained.

Nitration of 5-*Hydroxyflavone* (*I*, $R = H$, $R_1 = Ph$) *at* 100°: 5-*Hydroxy*-6: 8-*dinitroflavone* (*VI*, $R = H$, $R_1 = Ph$)

5-Hydroxyflavone (0·5 g.) in acetic acid (5·0 c.c.) was gradually treated with nitric acid (d. 1·42; 50 c.c.) when after about 5 minutes the mononitro derivative (III, R = H, R_1 = Ph) separated. The mixture was heated on a steam-bath for 15 minutes, when the mononitro product went in solution and the *dinitroflavone* (*VI*, $R = H$, $R_1 = Ph$) separated in tiny canary yellow plates, recrystallised from acetic acid, m.p. 253–54° (Found: N, 8·8. $C_{15}H_8O_7N_2$ requires N, 8·5%). It is sparingly soluble in boiling alcohol, insoluble in ether and benzene and easily soluble in acetic acid and acetone. It gives red coloration with alcoholic ferric chloride. With aqueous sodium hydroxide it gives an orange-yellow solution, while the sodium salt gets precipitated. *Acetyl* derivative, crystallised from acetic acid, m.p. 264–65° (Found: N, 7·8. $C_{17}H_{10}O_8N_2$ requires N, 7·6%).

The same dinitroflavone was also obtained on nitration of 5-hydroxy-6-nitroflavone[2] (V, R = H, R_1 = Ph) or 5-hydroxy-8-nitroflavone (III, R = H, R_1 = Ph) (0·5 g.) with nitric acid (d. 1·42; 5·0 c.c.) in acetic acid (10 c.c.) on a steam-bath for half an hour.

The dinitroflavone (VI, R = H, R_1 = Ph) (1·0 g.) was hydrolysed by 4 hours boiling with sodium hydroxide solution (2 N, 20 c.c.) when 2:6-dihydroxy-3:5-dinitroacetophenone (VII), m.p. and mixed m.p. 104° was obtained.

Nitration of 5-*Methoxyflavone* (*I, R = Me, R_1 = Ph*) *at* 0°: 5-*Methoxy*-8:(?)-*dinitroflavone*

5-Methoxyflavone (0·5 g.) was cooled to 0° (external) and a cooled mixture of sulphuric acid (5 c.c.) and nitric acid (5 c.c.; d. 1·42) was added gradually with stirring. It was kept at 0° for one and half hours and then poured into crushed ice. The nitro compound which separated was filtered, washed and crystallised from acetic acid, m.p. 267°. It analysed for a *dinitroflavone* derivative (Found: N, 8·4. $C_{16}H_{10}O_7N_2$ requires N, 8·2%). It did not give any coloration with alcoholic ferric chloride.

The same product was obtained even if the reaction mixture was kept for 20 minutes only. Attempts to get a mononitro derivative by treating the flavone (I, R = Me, R_1 = Ph) with (i) nitric acid (5 c.c.; 1·42) and acetic acid (5 c.c.) at 100° for half an hour or (ii) with fuming nitric acid (5 c.c.) and acetic acid (5 c.c.) at 100° for half an hour were fruitless. The original compound was recovered unaffected.

Attempts to demethylate the dinitroflavone with hydriodic acid and acetic anhydride or anhydrous aluminium chloride in nitrobenzene were unsucessful. Unlike 5-methoxy-8-nitrochromone, the dinitroflavone remained unaffected when kept with sodium hydroxide solution (10%) for 8 days or refluxed with alcoholic potassium hydroxide solution for 3 hours.

The dinitroflavone (0·5 g.) was refluxed with sodium hydroxide solution (10%; 90 c.c.) for 5 hours, when part of the substance got hydrolysed furnishing 2:6-dihydroxy-3-nitroacetophenone, m.p. and mixed m.p. 116–17°. The rest was recovered unchanged. No other product (nitrobenzoic acid) could be isolated from the reaction mixture.

Attempts to further nitrate this dinitroflavone met with failures.

SUMMARY

In extension of the previous work,[1] nitration of 5-hydroxy-2-methylchromone, 5-hydroxyflavone and their methyl ethers has been investigated.

The mono derivatives from the hydroxychromones have been found to be the 8-nitro compounds, while the di-derivatives were 6: 8-dinitro products. The constitutions of the mononitro derivatives have been assigned as they were different from the products, obtained on Kostanecki acylations of 2: 6-dihydroxy-3-nitroacetophenone and subsequent deacylation of the 3-acyl derivatives, which would be expected to be the 6-nitro chromones. The constitutions of dinitro derivatives were established by alkaline hydrolysis. 5-Methoxy-2-methylchromone gave 8-nitro derivative, as on demethylation the corresponding hydroxychromone was obtained. On further nitration demethylation occurred furnishing 5-hydroxy-2-methyl-6: 8-dinitrochromone. 5-Methoxy-flavone gave a dinitro derivative to which has been provisionally given the structure 5-methoxy-8-(?)-dinitroflavone.

The authors are grateful to Dr. S. M. Sethna for his keen interest in the work.

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXIX. A Method for the Reduction of 5:7-Dihydroxyflavones to 5-Hydroxyflavones

BY V. RAMANATHAN AND K. VENKATARAMAN, F.A.SC.

(Department of Chemical Technology, University of Bombay)

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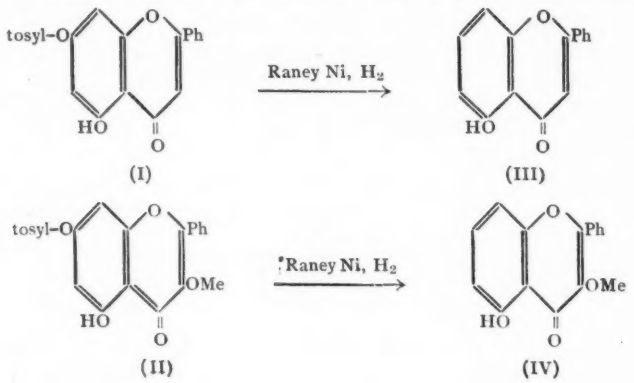
5-HYDROXYFLAVONE, which occurs together with flavone in the meal or dust of the leaves and stems of *Primula imperialis*,[1] was first synthesized by Sugasawa[2] by the Allan-Robinson reaction on 2-acetylresorcinol, and later by the transformation of 2: 6-dibenzoyloxyacetophenone to the corresponding diketone, followed by cyclization.[3] 5-Hydroxyflavonols have been prepared by Seshadri[4] by the Kostanecki method from 2-hydroxy-6-methoxyacetophenone *via* the chalkone, flavanone and isonitrosoflavanone.

In the course of our work on Raney nickel reductions it was observed that an application of the method of Kenner and Murray[5] for the cleavage of sulphonic esters with Raney nickel leads to a convenient method for the preparation of γ-resorcylic acid by the hydrogenolysis of the mono-*O*-*p*-toluenesulphonyl derivative of phloroglucinol carboxylic acid.[6] Extending this procedure to the flavone series, we have converted chrysin (5: 7-dihydroxyflavone) to 5-hydroxyflavone and galangin 3-methyl ether (5: 7-dihydroxy-3-methoxyflavone) to 5-hydroxy-3-methoxyflavone. A general method has thus become available for the synthesis of 5-hydroxyflavones, which are of



interest because of their possible occurrence in nature and also as intermediates for the synthesis of naturally occurring 5:8-dihydroxyflavones by the Elbs-Seshadri persulphate oxidation.

Chrysin[7, 8] and galangin 3-methyl ether[9] readily gave the 7-*p*-toluenesulphonyl esters (I and II) on treatment with a molar proportion of *p*-toluenesulphonyl chloride and excess of anhydrous potassium carbonate in boiling acetone. It was necessary to carry out the hydrogenolysis of the tosyl derivatives under controlled and mild conditions, leaving a part of the tosyl derivative unreacted to poison the nickel catalyst in order to avoid undesirable side reactions. The crude reaction mixture was treated with alcoholic caustic potash to hydrolyse the unreacted tosyl derivative and the mixture of hydroxyflavones separated by chromatography. Thus by the hydrogenolysis of the 7-tosyl ester (I) of chrysin, a mixture of 5-hydroxyflavone (III) and chrysin was obtained; when the mixed flavones were dissolved in benzene and chromatographed on Florex xxx (an extruded fuller's earth supplied by the Floridin Co., Inc.), development and elution with benzene yielded 5-hydroxyflavone (III) in a yield of about 25 per cent. calculated on the quantity of the tosyl derivative (I) consumed in the reaction. Elution with ethyl acetate then led to the recovery of the more strongly adsorbed chrysin. In the case of the 7-tosyl ester (II) of galangin 3-methyl ether Raney nickel treatment and hydrolysis of the product yielded galangin 3-methyl ether and 5-hydroxy-3-methoxyflavone (IV), readily separable by chromatography. It was found, however, that galangin 3-methyl ether and 5-hydroxy-3-methoxyflavone can be separated in a simpler manner by taking advantage of the sparing solubility of the former in benzene. Methylation of (IV) gave 3:5-dimethoxyflavone, m.p. 119–20°. The m.p. quoted by Seshadri[4] for 3:5-dimethoxyflavone is 160–2°. The possibility of our compound (IV) and its methyl ether being flavanones was eliminated by Wilson's boric-citric acid test[10] to which (IV) responded, and by treatment of the dimethyl ether with selenium dioxide in boiling xylene;[11] most of the starting material was recovered unchanged, a small part undergoing oxidation to a brown oily substance. Further, the production of 5-hydroxyflavone by the reduction of the tosyl derivative of chrysin and the recovery of chrysin and of galangin 3-methyl ether in the two reduction experiments left little doubt that 5-hydroxy-3-methoxyflavone and 3:5-dimethoxyflavone obtained by us had the authentic structures assigned to them. It was also observed that quercetin and its pentamethyl ether were substantially unaffected by Raney nickel under the specified conditions. However, in view of the discrepancy in the melting points cited for 3:5-dimethoxyflavone, an alternative synthesis has been undertaken, based on the method reported by Karmarkar, Shah and one of

us for the preparation of 2-phenylacetylresorcinol (2:6-dihydroxyphenyl benzyl ketone).[1,2]

EXPERIMENTAL

5-*Hydroxy*-7-*tosyloxyflavone* (*I*)

Chrysin (2 g.) was dissolved in dry acetone (100 c.c.), *p*-toluenesulphonyl chloride (1·5 g., 1 mol.) and anhydrous potassium carbonate (10 g.) were added, and the mixture refluxed for 3 hours. The acetone was distilled off, the residue taken up in water and acidified. The precipitate was filtered, washed with water, dried and crystallized from alcohol; the yellow rectangular plates (2·88 g.) had m.p. 166° (Found: C, 64·7; H, 4·3. $C_{22}H_{16}O_6S$ requires C, 64·7; H, 3·9%). The substance gives with dilute aqueous caustic soda a yellow sparingly soluble sodium salt, and with alcoholic ferric chloride a red-violet colour.

Reduction of 5-*hydroxy*-7-*tosyloxyflavone*

5-Hydroxy-7-tosyloxyflavone (I: 1 g.) was dissolved in alcohol (500 c.c.) Raney nickel (7 g.) was added, and the mixture agitated at room temperature for one hour while a steady stream of hydrogen was led in. The mixture was then filtered. The alcoholic filtrate was concentrated to 20 c.c. The nickel residue was deactivated under hydrochloric acid, filtered and the residue was extracted with ether. The product obtained after the removal of ether was added to the alcohol concentrate, caustic potash (0·5 g.) dissolved in a few drops of water was added, and the mixture refluxed for one hour. On removal of the alcohol the residue was taken up in water and acidified. The precipitate (0·32 g.) was dissolved in benzene and chromatographed on Florex xxx. Elution with benzene and evaporation of the yellow percolate gave yellow needles, which were recrystallized from alcohol (yield 0·12 g.). The m.p. was 157°, undepressed when mixed with 5-hydroxyflavone prepared from 2-acetylresorcinol dibenzoate.[3] Further elution with ethyl acetate yielded chrysin (0·11 g.).

5-*Hydroxy*-3-*methoxy*-7-*tosyloxyflavone* (*II*)

Galangin 3-methyl ether (3·5 g.), *p*-toluenesulphonyl chloride (2·4 g; 1 mol.), anhydrous potassium carbonate (15 g.), and acetone (250 c.c.) were refluxed for 3 hours. The acetone was then removed, the residue taken up in water and acidified. The yellow precipitate was collected, washed and dried, and it crystallized from alcohol in yellow needles (4·5 g.), m.p. 156–57° (Found: C, 63·4; H, 4·4. $C_{23}H_{18}O_7S$ requires C, 63·0; H, 4·1%). The substance gives with aqueous caustic soda a sparingly soluble yellow sodium salt, and with alcoholic ferric chloride a red-violet colour.

Reduction of 5-hydroxy-3-methoxy-7-tosyloxyflavone

The tosyl ester (II; 3 g.) was dissolved in alcohol (1,500 c.c.), Raney nickel (21 g.) added, and the mixture agitated for one hour while a steady stream of hydrogen was led in. The mixture was then filtered and concentrated to 40 c.c. The nickel residue was deactivated under hydrochloric acid, filtered and the residue extracted with hot alcohol. The extract was added to the above concentrate, potassium hydroxide (1·5 g.) dissolved in a small amount of water added, and the solution refluxed for one hour. The alcohol was distilled off, the residue taken up in water and acidified. The precipitate (1·62 g.) was extracted with cold benzene, and the benzene extract chromatographed on Florex. The yellow percolate on evaporation gave a yellow substance, which crystallized from methanol in yellow elongated prisms (0·82 g.), m.p. 115° (Found: C, 71·5; H, 4·9. $C_{16}H_{12}O_4$ requires C, 71·7; H, 4·5. The m.p. quoted by Seshadri is 115–16).[13] 5-Hydroxy-3-methoxyflavone (IV) gives a difficultly soluble yellow sodium salt with aqueous caustic soda, and with alcoholic ferric chloride a violet colour which develops a slightly greenish tinge. On treatment with magnesium and hydrochloric acid the substance gives an orange-red colour. With Wilson's boric-citric acid-acetone reagent it gives a yellow colour like 5-hydroxyflavone and quercetin.

The residue unextracted by benzene (0·62 g.), after crystallization from ethyl acetate was identified as galangin 3-methyl ether by m.p. and mixed m.p.

3: 5-*Dimethoxyflavone*

5-Hydroxy-3-methoxyflavone (0·3 g.) was treated with dimethyl sulphate (1 c.c.) and anhydrous potassium carbonate (3 g.) in boiling acetone (20 c.c.) for 12 hours. The mixture was filtered and the residue washed with acetone. Evaporation of the solvent gave a colourless substance which crystallized from aqueous methanol in long colourless plates, m.p. 119–20° (Found: C, 72·1; H, 5·1. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). The substance is insoluble in dilute caustic soda solution and gives no colour with alcoholic ferric chloride.

The substance (0·3 g.) was dissolved in xylene (10 c.c.) selenium dioxide (0·3 g.), added and the mixture refluxed for 12 hours. On cooling, selenium was filtered off and washed with ether. The xylene and ether were removed by steam distillation and the brown residue was dissolved in benzene and chromatographed on alumina. The pale yellow eluent gave a minute amount of a brown oil. On further elution with alcohol, a yellow percolate was

obtained which on concentration gave an oil. The oil solidified on contact with methanol, and crystallized from aqueous methanol in colourless elongated plates (0·25 g.), m.p. 119–20°, undepressed when mixed with the starting material.

SUMMARY

A general method for the preparation of 5-hydroxyflavone and its derivatives from the corresponding 5: 7-dihydroxyflavones by the action of Raney nickel on the 7-tosyloxy derivatives is described. Thus chrysin has been converted into 5-hydroxyflavone, and galangin 3-methyl ether to 5-hydroxy-3-methoxyflavone.

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CHEMISTRY OF THE THIAZOLES

Part V. Fine Structure and Orientation

By K. Ganapathi, F.A.Sc. and K. D. Kulkarni
(*Department of Chemotherapy, Haffkine Institute, Parel, Bombay*)

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1. Introduction

The thiazole ring system from the point of view of fine structure remains the least studied of the heterocyclic compounds. None of the customary physical or physico-chemical measurements which give us accurate ideas about the dispositions of the various atoms in the ring, the bond distances, the valency angles and the state of polarisation of the atoms, have been made with thiazole or any of its derivatives. So, to understand the fine structure of the thiazole derivatives, we have to rationalise *a posteriori* on the basis of the physical properties and the chemical reactivities of the various thiazole derivatives so far reported. This paper is an attempt in this direction.

2. Polarisation (Mesomerism) and Disposition of the Atoms in the Ring

There are some very characteristic properties of thiazole and its derivatives which should be reflected in their fine structure. Though thiazole is a five membered heterocyclic compound, in its properties such as the boiling point, basicity, solubility in water, odour, reactivity, isosterism and resistance to the attack of electrophilic reagents, it strikingly resembles the six-membered compound pyridine and also pyrimidine, and sharply differs from the five-membered heterocyclic compounds, thiophene, furan, oxazole, glyoxaline and pyrrole. There are some thiazole derivatives which, in their properties and behaviour, resemble the corresponding thiophene, furan, or glyoxaline derivatives rather than the pyridines. Next, the thiazole compounds fall into two groups: the first consists of thiazole and some derivatives which are stable and resist attack by electrophilic reagents, while the second group comprises of derivatives which show properties quite the reverse of this. Thirdly, in some substitution reactions, even with the reagents of the same category, there is a difference in the orientation of the incoming group; in the case of nitration and sulphonation, the position taken by the incoming group is different from that in halogenation. Lastly, the reactivities of the various groups or atoms present in thiazoles differ

markedly depending upon the position they occupy in the ring and also upon the substituents in the other positions.

To seek an explanation for these properties, one of the methods adopted is to rely on the resonant structures. Erlenmeyer *et al.*[1] studied the deuterium and hydrogen exchange in 4-methylthiazole-5-carboxylic acid and postulated that thiazole exists in the resonant forms represented by the formula (I) and express the view that this postulation provides an explanation for an aromatic linkage between the carbon atoms 4 and 5 and for an "aromatic sulphur", *i.e.*, a sulphur atom that does not behave as a thioether. On the basis of the general rules available for the postulation of the

(I)

resonant structures and on analogy with the structures proposed for the other heterocyclic ring systems, we could write down a number of resonant formulæ for thiazole also. But this does not help us because we cannot assess the contributions of the various forms due to lack of data to calculate the resonance energies, bond distances, or the character of the various bonds. On the other hand, we can get far ahead by examining the mesomeric influences in the thiazole ring, the polarisation of the various atoms, the nature of the bonds, and the effects of the substituents in the ring as revealed by the experimental results, as is shown below:

The system N—C_2—S.—This system is taken together since these three atoms individually influence the properties of the other. Of the two heterocyclic atoms, nitrogen dominates in governing the properties of thiazole which is evidently because it has the lesser number of unshared electron pairs than sulphur.[2] Depending upon the nature of the substituents at C_2, the ring nitrogen can function in two diametrically opposed roles, *viz.*, (i) as an electron sink when the substituent at C_2 is an electron acceptor (nitro, carboxy, carbonyl, sulphonic, or cyano groups) or cannot tautomerise with the nitrogen (hydrogen, halogens) and (ii) as an electron source or a relay of electrons when the substituent at C_2 (amino, substituted amino, hydroxy, substituted hydroxy, mercapto, substituted mercapto groups) is an electron donor or can tautomerise with nitrogen (hydroxy, mercapto and amino groups). These two possibilities as regards the function of nitrogen account for the two types of effects resulting in the segregation of the thiazoles into the abovementioned two classes as shown below:

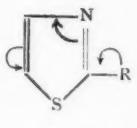
(i) In the first case, due to the electron attraction (−T effect) of the ring nitrogen (II), there is a deactivation of the thiazole nucleus to the substitution by electrophilic reagents, just as in pyrimidine[3] or pyridine.[3] The carbon atom 2 which becomes kationoid in reactivity can however make up its electron defect to some extent from the sulphur atom, the system thus becoming a partially neutralised one.[4] As a result, C_2 is not attacked by electrophilic reagents but is capable of attack by nucleophilic reagents. In addition, the substituent at C_2 shows properties of one attached to a carbonyl or a carboxyl group[5]—*e.g.*, the 2-methyl group in 2-methyl-4-phenylthiazole, 2-methylthiazole, 2:4-dimethylthiazole react with formaldehyde, chloral or aromatic aldehyde[6, 7, 8] and is also easily oxidised[9]; the 2-halogenothiazoles are easily attacked by nucleophilic reagents[10, 11]; the 2-carboxylthiazoles are easily decarboxylated[12, 13, 14]; the 2-aminothiazoles do not form Schiff's bases, nor undergo diazotisation and Sandmeyer's reaction under ordinary conditions[15, 16] typical of the aromatic amines.

(ii) In the second group of thiazoles, the ring nitrogen acts as an electron donor (III or IV) or a relay of electrons (V) and leads to electron density (availability of π electrons) at C_5 which is thus attacked easily by electrophilic reagents. Such derivatives of thiazole stand as a contrast to those of the first group; they are very reactive and are not as stable as those of the former group; the 2-aminothiazoles gradually darken and decompose and the 2-hydroxythiazoles polymerise. In these derivatives, the atoms or groups at C_5 are activated so that they react with comparative ease with nucleophilic reagents.

(II)

(III)

(IV)



(V)

Carbon atom 4.—The carbon atom 4 is attached to nitrogen by a single bond and there is no reaction known in which we can postulate a double bond between C_4 and nitrogen. This fact casts doubt on the physical basis of the resonant structures wherein there is a double bond between C_4 and nitrogen. We find a distinct difference in properties of the atoms or groups attached to C_2 and C_4—*e.g.*, the methyl groups[6, 7, 8] and halogens[20, 21, 22] attached to C_4 are inert; the 4-carboxylthiazoles are the most resistant of the lot to undergo decarboxylation[12, 13, 17]; the 4-aminothiazoles are not at all stable,[18, 19] while the 2-aminothiazoles are comparatively the stablest of the lot.[18]

The double bond between C_4 and C_5.—The bond connecting C_4 and C_5 does not behave as an aliphatic double bond. It does not add on halogens or get easily hydrogenated. It undergoes substitution at C_4 or C_5 depending upon the activation mechanism. The chlorine or bromine atoms at C_4 and C_5 are comparatively inert[20, 21, 22] unless activated by other groups. The 5-aminothiazoles behave as typical aromatic amines[23, 24, 25] (while the 2-amino and 4-aminothiazoles do not), being diazotisable under normal conditions and capable of formation of Schiff's bases.

The double bond is attached to the two heterocyclic atoms nitrogen and sulphur, of which the sulphur functions always as the electron donor. On the other hand, nitrogen, as shown above, can function in two capacities depending upon the nature of the substituent at C_2; in either case, the effect due to sulphur is suppressed. In the isolated heteroenoid system (VI), the polarisation due to sulphur should lead to electron density at C_4. But this is counteracted by the attachment of C_4 to nitrogen. When the nitrogen functions as an electron sink, there is internal neutralisation as shown in (VII) and no substitution occurs at C_4. On the other hand, when nitrogen acts as an electron source or relay of electrons, polarisation as shown in (III), (IV) or (V) takes place leading to activation of C_5 and thus the effects due to sulphur and nitrogen cross. Since nitrogen is more anionoid than sulphur,[2] the effects due to nitrogen win out and substitution occurs at C_5 and not at C_4. We thus realise how thiazole differs from thiophene as regards substitution.

(VI)

(VII)

The comparative effects at positions 2, 4 *and* 5.—Unlike the other heterocycles, the positions 2, 4 and 5 in thiazole are not alike and we should have some idea about the relative electron densities at these three positions. Calculations by quantum mechanical theories have been made in analogous cases,[25a] but we are not competent to pass remarks on these, except that these calculations have to take into account a number of factors that contribute to the electron densities in the heterocyclic system. The experimental evidence for this could be sought for in two directions: (*a*) by comparison of the physical and chemical properties of a series of isomeric thiazoles having the same substituent at the three positions, and (*b*) by substitution

reactions. The data available presented in the following table, does not furnish an unequivocal answer to this question.

The melting point of a compound is a result of a number of complex factors[28] and only in very straightforward cases could it be taken as an indication of the electron mobilities. We find that in the acetamidothiazole series, the order of increasing melting point is $2 > 4 > 5$. On the other hand, in the carboxylic acid series, it is reversed, namely, $5 > 4 > 2$ (it should be noted that the electronic effects of the acetamido and the carboxyl groups are of opposing nature). As regards the ease of decarboxylation of the thiazole carboxylic acids, the sequence is $2 > 5 > 4$ and it should be noted also that decarboxylation can take place by more than one mechanism.[29] The stability of the aminothiazoles and the reactivities of the halogenothiazoles to attack by nucleophilic reagents also point to the sequence $2 > 5 > 4$.

Comparison of the physical properties and reactivities of the isomeric thiazoles

Position of substituent	2	4	5	Order
Methylthiazole, b.p.	127·5–28°/ 729 mm.	133–4° 131–2°	141–2°	5>4>2
Phenylthiazole, b.p.	267–9°/ 732 mm.	273°	?	
m.p.	?	52°	45–6°	
picrate, m.p.	124–5°	164–5°	138–9°	4>5>2
Aminothiazole, m.p.	90°	?	83–4°	2>5
Acetamidothiazole, m.p.	203°	175–6°	159–60°	2>4>5
Thiazolecarboxylic acid, m.p.	102°	196–7°	218°	5>4>2
Ease of decarboxylation of the acids				2>5>4
Stability of the aminothiazoles				2>5>4
Reactivity of the halogenothiazoles				2>5>4
Reactivity of the Me groups				2>5/4
Ease of hydrolysis of acetamidothiazole				2>5
Substitution in nitration and sulphonation				5>4>2
Halogenation				2>5/4
Anionoid substitution (picrylchloride)				2>4>5

In the case of substitution reactions, the halogenation of thiazole could have given the clue. But this does not proceed on under normal conditions. Thiazole has been brominated only at high temperatures to 2-bromothiazole.[26] Since bromination at high temperature is a complex reaction,[27] unless we have information as to the nature of the radical that attacks thiazole, we cannot jump to the conclusion that the electron density is maximum at the position 2. Thiazole has been sulphonated to thiazole-5-sulphonic acid, but in this case, as would be shown later on, it is the thiazolium ion that undergoes substitution. As regards substitution by picrylchloride, it is also the ion that undergoes substitution.

On the whole, we recognise two sequences 2, 4, 5 as regards the melting points and substitution of the thiazolium ions, and 2, 5, 4 for the reactivities of the compounds. Unless more systematic work is done in this direction, we have to reserve judgment on this issue.

3. SUBSTITUTION IN THE THIAZOLES

The Japanese workers were the first to carry out systematic work on the problem of substitution in the thiazole derivatives and they have made some generalisations. But they have used only the disubstituted thiazoles, so that the entering group has no choice as regards the position of substitution. They rely on the ease of substitution for deciding the orienting influences. Schofield[30] who has dealt with substitution in the heterocyclic derivatives has not considered the thiazoles at all.

In the case of the benzene derivatives, the substitution is decided by two factors: (i) the nature of the substituent already present, whether it is electron attracting or electron releasing, and (ii) the nature of the reagent used for substitution, whether it is electrophilic (kationoid) or nucleophilic (anionoid). In the heterocyclic compounds, wherein all the atoms in the ring are not identical as in benzene, the problem becomes more complex. In addition to the influence of the substituents, the polarisation of the ring itself due to the hetero atoms has also to be taken into account and we have no quantitative method of gauging which of the effects would win out in case they are of opposing nature. Then there is the question of the part played by the reagent used for substitution. If the hetero atom of the ring is capable of quaternary salt formation with the reagent used, then the directive effect of this ion is to be taken into account, so that this necessitates the subclassification of the electrophilic or nucleophilic reagents depending whether they form salts or not with the compounds attacked.

3.1. Substitution by Electrophilic (Kationoid) Reagents

In the case of the thiazoles, the abovementioned complex situation prevails. Of the electrophilic reagents that are employed, namely, nitric acid, sulphuric acid, halogens, diazonium salts, nitrous acid, benzaldehyde, formaldehyde, etc., the first two are capable of formation of quaternary salts with the thiazole ring nitrogen (protonisation), while the others are not. This introduces an important difference in mechanism between nitration and sulphonation on the one hand from the other substitution reactions.

3.1.1. Substitution by Electrophilic Reagents—Nitration and Sulphonation

In these two cases, it is the thiazolium ion (VIII) that undergoes substitution and the one single factor that appears to govern the orientation is the positive pole, nitrogen. So, for the entering group, the first choice is that position farthest removed from nitrogen, namely C_5. Of the remaining two positions, C_4 should be more negative than C_2, since nitrogen is attached to C_2 by a double bond, which means that the position 4 would be preferred more than C_2. So, the orientation sequence for nitration and sulphonation should be $C_5 > C_4 > C_2$. This is what is observed. In the orientation of the incoming group, the influence of the positive pole dominates irrespective of the influence of the substituent in the ring and thus this resembles what is observed in the furan and thiophene compounds.[31] However, the effect of the substituent already present in the compound comes into play only as regards the speed of substitution. If the orienting effect of the group present and that of the pole lead to the same result, substitution takes place with great ease; but if they are of opposing nature, the substitution is either difficult or does not take place at all. The general principle in aromatic substitutions, that the groups that are electron acceptors slow down the substitution rate while the electron donors increase the speed, holds good here also. The above deductions are confirmed by the data available so far.

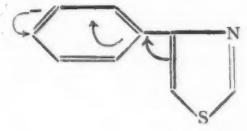
Thiazole is not nitrated even at temperature of the boiling water-bath.[20] If the nitration is carried out under more drastic conditions as in the case of pyridine,[32] we can predict the formation of 5-nitrothiazole. Thiazole has been sulphonated at 250° C. to thiazole-5-sulphonic acid. Thus thiazole resembles pyridine rather than thiophene or furan which undergo substitution very readily or are decomposed by acids[34] by violent reactions.

2-Methylthiazole (the methyl group showing a weak + I effect) undergoes nitration only with difficulty to furnish 2-methyl-5-nitrothiazole in about 4 per cent. yield.[11, 35] 2-Hydroxythiazole,[35] 2-aminothiazole,[20] and 2-acetamidothiazole[20] (wherein the substituents are strong electron donors)

undergo substitution with great ease to furnish the 5-nitro derivatives. In addition, 2-aminothiazole on sulphonation furnishes the 5-sulphonic acid derivative,[33] 2-hydroxy-4-methylthiazole,[36] 2-amino-4-methylthiazole,[20, 32] 2-acetamido-4-methylthiazole,[20] and 2:4-dimethylthiazole,[20] all undergo nitration to yield the corresponding 5-nitro derivatives and on sulphonation furnish the 5-sulphonic acid derivatives. On the other hand, 2-chlorothiazole,[20] and 2-nitrothiazole[37] do not undergo nitration or sulphonation. 2-Bromothiazole, which could not be nitrated,[20] has been sulphonated under drastic conditions to 2-bromothiazole-5-sulphonic acid.[33]

4-Methylthiazole furnishes 4-methylthiazole-5-nitrothiazole on nitration[38, 39] and 4-methylthiazole-5-sulphonic acid on sulphonation.[36] Thus it is clear that position 5 is preferred to position 2 by the entering group. 4-Phenylthiazole[10] gets substituted in the benzene ring rather than in the thiazole nucleus; this could be interpreted to mean that benzene undergoes substitution more easily than thiazole and the polarisation in this case being as shown in (IX). While 4:5-dimethylthiazole furnishes the 2-nitrothiazole derivative, 4-phenyl-5-methylthiazole also gets nitrated in the benzene nucleus.

(VIII)



(IX)

5-Methylthiazole could be nitrated only with difficulty furnishing 4-nitro-5-methylthiazole.[11, 38] The nitration of 2-amino-5-methylthiazole has been reported a failure[38]; probably more drastic conditions are required. 2-Acetamido-5-methylthiazole, however, furnishes 2-acetamido-4-nitro-5-methylthiazole.[38] 2:5-Dimethylthiazole on nitration and sulphonation have been reported to furnish the 4-substituted product.[38] In the nitration of 2-acetamido-5-bromothiazole, instead of the nitro group entering the position 4, it replaces the bromine atom at C_5, furnishing 2-acetamido-5-nitrothiazole,[43] analogous to what happens in the thiophene series.[44] Garreau[41] has shown that bromine atom in these positions to be positive like hydrogen and hence we can anticipate the replacement by the nitro group. When a strong electron donating group (amino, acetamido, or methoxy) is present at C_5, it activates the position 4 and 2 and nitration in such cases is facile. 5-Acetamidothiazole undergoes nitration with ease to furnish 5-acetamido-4-nitrothiazole.[35, 37] 2-Benzyl-5-acetamidothiazole[24] and 2-methyl-5-ethoxythiazole get nitrated with ease to furnish the 4-nitrothiazoles.

In all the nitrations dealt with above, it should be noted that it takes place through the thiazolium ion as a result of the reagent forming a salt with the molecule attacked. On the other hand, if nitration would be effected with a reagent that does not form a salt,[41a] the mechanism should be different and we can expect differences in the orientation of the incoming group in some cases.

3.1.2. Substitution by Other Electrophilic Reagents

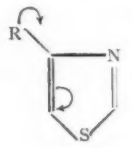
In the case of substitution by other electrophilic reagents that do not form salts with nitrogen, the orientation is decided by the influence of the substituent present, and also by the polarisation of the ring.

Thiazole, as shown before, is resistant to attack by electrophilic reagents. It cannot be halogenated at ordinary conditions. On bromination in the vapour phase, thiazole yields 2-bromothiazole and 2: 5-dibromothiazole.[26] Other reactions with thiazole have not been tried.

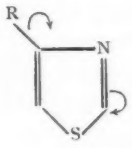
As far as the substitution at the position 2 is concerned, an electron donor always activates the position 5 as shown in (IV) or (V), while the electron acceptor reduces the speed of substitution or completely stops it. The halogens, while they create electron density at C_5, reduce the speed of substitution due to the inductive effect. 2-Methylthiazole undergoes bromination only with difficulty to yield 2-methyl-5-bromothiazole.[35] On the other hand, 2-aminothiazole,[33, 45, 46, 47] 2-acetamidothiazole,[48] 2-hydroxythiazole,[35] all undergo halogenations to furnish the 5-halogenothiazoles. 2-Nitrothiazole[37] and 2-chlorothiazole[15] could not be brominated. However, 2-bromothiazole, which could not be brominated under ordinary conditions, furnishes 2: 5-dibromothiazole in the vapour phase.[26] While 2-amino-5-methylthiazole[38] and 2: 5-dibromothiazole[38] do not get brominated, 2-aminothiazole, 2-amino-4-methylthiazole,[45, 50] 2: 4-dimethylthiazole[18] and 2-hydroxy-4-methylthiazole[50] all get brominated to yield the 5-bromo derivatives. This shows that the bromine atom is reluctant to enter the position 4. 2-Aminothiazole couples with diazonium salts.[16, 20, 49] Similarly, 2-hydroxythiazole[35] and 2-hydroxy-4-methylthiazole[20] couple with diazonium salts. But 2-amino-4-methylthiazole[18] and 2: 4-dimethylthiazole do not couple. 2-Hydroxythiazole[35] and 2-hydroxy-4-methylthiazole[52] react with acetic anhydride furnishing the corresponding 5-acetylthiazole derivatives. Mannich reaction (formaldehyde and dimethylamine) has been found to be successful with 2-acetamidothiazole and 2-acetamido-4-methylthiazole furnishing 5-dimethylaminomethyl derivatives[51]; on the other hand, 2: 4-dimethylthiazole gives only a trace of a product. Mercuration and thiocyanation have been reported with 2-acetamidothiazole and other derivatives to furnish

the 5-substituted products[13]; but these reactions are quite likely to be free radical substitution reactions rather than substitution by electrophilic reagents.

As regards the 4-substituted thiazoles, the data available is scanty, though compounds of this class are of great importance to decide some crucial issues. While we could expect the 4-carboxy, nitro (not known so far), and 4-bromo (not so far) thiazoles not to undergo substitution, as regards the others (acetamido-; ethoxy thiazoles), the orientation is difficult to predict, whether it would lead to the activation of the position 2 or 5, as shown in (X) and (XI). 4-Methylthiazole does not undergo bromination



(X)

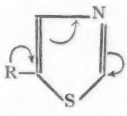


(XI)

under the usual conditions.[50] Treatment of 4-methylthiazole with benzaldehyde has been reported to lead to the 2-substituted product.[53]

Among the 5-substituted derivatives, not many cases have also been studied. It is in such derivatives that the orientation between nitration and sulphonation differ from the halogenations. Of the two positions 2 and 4 available for substitution, in nitration and sulphonation the position 4 is preferred. In the halogenations, the position 2 is chosen by the entering group. But if there is a strong electron donating group present at the position 5, there is activation of the position 4 also so that we get 2: 4-disubstituted products, the mechanisms (XII) and (XIII) operating evidently. 5-Methylthiazole on bromination furnishes 2-bromo-5-methylthiazole.[35] On boiling 5-methylthiazole with benzaldehyde, 2-substituted product is obtained.[8, 54] 5-Acetamidothiazole on bromination furnishes, even with one molecular equivalent of bromine 2: 4-dibromo-5-acetamidothiazole.[35, 57]

(XII)



(XIII)

5-Amino-2-benzylthiazole undergoes easily diazo coupling.[24] 5-Ethoxy-2-methylthiazole gets easily brominated to furnish the 4-bromo derivative.[22]

3.2. Substitution by Nucleophilic (Anionoid) Reagents

The reagents that are in vogue as representatives of this class are: sodamide, active anions (NH^-, OH^-, CN^-, etc.). In the case of the thiazoles, picrylchloride and 2:4-dinitrochlorobenzene have been tried.

The reaction with sodamide has been reported in only one case 4-Methylthiazole yields with sodamide 2-amino-4-methyl-thiazole.[36] But it is known that sodamide adds on to the carbon nitrogen double bond as a preliminary to substitution.[55] If this be the case, the use of this reaction as a gauge of the electron density at the various positions is of limited applicability.

The reaction with picrylchloride has been well studied with a number of thiazoles.[56] In these cases, the initial product formed is reported to be a quaternary salt which subsequently undergoes substitution. So, here also, as in the case of nitration, it is the thiazolium ion that decides the orientation of the incoming group. Since the present case is a substitution by the nucleophilic reagent, the order preference for the various positions should be the reverse of that for the electrophilic reagents and hence should be $2 > 4 > 5$.

The results obtained are best interpreted on this basis. McLean and Muir[56] have treated thiazole, 2-methylthiazole, 5-methyl-thiazole, 2:4-dimethylthiazole and 2:5-dimethylthiazole with picrylchloride and have studied the products obtained. Though the actual orientations have not been studied experimentally, the results obtained could be interpreted convincingly. Thiazole gives easily a picryl derivative, as contrasted with the difficulty of nitrating and brominating thiazole. The substitution compound has been assigned the structure of 2-picryl thiazole, because all the thiazoles in which the position 2 is free undergo substitution easily. Thus, 5-methylthiazole also easily gives the picryl derivative while 2-methylthiazole gives no substitution product at all. While 2:4-dimethylthiazole did not give a substitution product, 2:5-dimethylthiazole does yield a substitution product though not as easily as thiazole or 5-methylthiazole. 4-Methylthiazole and 2:4-dimethylthiazole did not even form the quaternary salts. The above results could be explained convincingly if we assume the order $2 > 4 > 5$ for the reactivity of the nucleophilic reagents.

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CHEMISTRY OF THE THIAZOLES

Part VI. Chrysean and Some of Its Derivatives

By K. Ganapathi, F.A.Sc. and K. D. Kulkarni

(*Department of Chemotherapy, Haffkine Institute, Bombay*)

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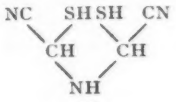
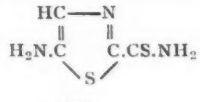
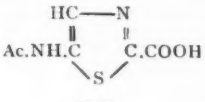
What appears to be the first thiazole compound appears to have been prepared inadvertently by Wallach[1] in 1874 by the extremely simple operation of passing hydrogen sulphide into a concentrated solution of sodium cyanide expecting to get thioformamide. Instead, he got a golden yellow compound which he called 'chrysean' invoking its brilliant golden colour. Twenty-five years later, Hellsing[2] studied this compound. He first assigned this compound the structure (I) which, some time later, he revised to 2-thioamido-5-aminothiazole (II). As the final degradation product he obtained a



(I)



(II)



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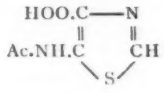


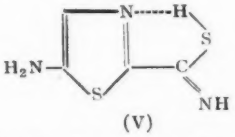
(IV)

acetamido compound which he reasoned out should be 5-acetamidothiazole. This has been confirmed by the synthesis of 5-acetamidothiazole by Erlenmeyer *et al.*,[3] starting from ethyl thiazole-5-carboxylate according to the method developed by Ganapathi and Venkataraman.[4] That chrysean cannot be 5-amino-4-thioamidothiazole has been proved by the fact that 5-acetamino-4-carbethoxythiazole synthesised by Cook *et al.*[5] is not identical with the acetamidothiazolecarboxylic acid obtained from chrysean, which should therefore be 5-acetamidothiazole-2-carboxylic acid. While the structure (II) of chrysean is undoubtedly correct, it has not yet been synthesised. A number of attempts made by Ganapathi and Venkataraman to synthesise chrysean or 5-acetamido-2-cyanothiazole were not successful.

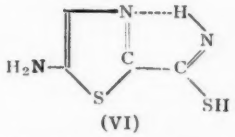
We present here our work on chrysean, its probable mode of formation and the compounds we have prepared making use of the two reactive groups in the compound.

It has been reported by previous workers, as also by Arnold and Scaife,[6] that chrysean has the m.p. 204°. But by repeated crystallisation of the product we have been able to obtain two compounds, one separating in golden yellow plates, m.p. 222°, and the other, more soluble and obtainable in only small quantities, separating in needles, m.p. 146–46·5°. The mixed melting point of the two is anywhere between the two figures. They give the same acetyl compound and yield on degradation 5-acetamidothiazole. Existence of two compounds in the thiazoles has been reported in the case of sulphathiazole, which can be isolated in two forms, m.p. 176° and 202° and in the case of thiamine chloride which is known to exist in two forms, m.p. 232-4° and 249–50°. As regards the last, William and Cline[7] think that the two forms are stereoisomers, while Todd and Bergel[8] consider them to be due to dimorphism, because both are interconvertible.

Now the question arises whether the two forms of chrysean isolated are stereoisomers or dimorphs. While this could be settled only by physical measurements, we wish to discuss the theoretical possibilities. Because of the presence of the double bond between the carbon atoms 4 and 5 of the thiazole nucleus, these two carbon atoms, their fourth valencies, the nitrogen and sulphur atoms should all lie in the same plane. As regards the carbon atom 2, there are two possibilities: either it can lie in the same plane as the others or can be slightly out of plane. Since this carbon has only one valency free, the possibility of stereoisomerism is not there in the second case, unless there is restricted rotation of the group attached to the carbon atom 2. But there is a distinct possibility of two isomers in the case of chrysean if we take into account the possibility of hydrogen bond formation between the ring nitrogen with the hydrogen attached to the mercapto or the imino group, as shown in (V) and (VI). We hope to decide this question soon.



(V)



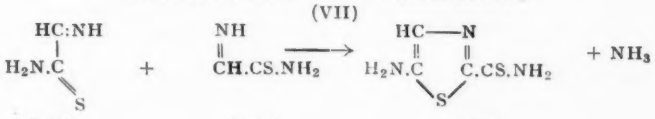
(VI)

As regards the formation of chrysean by the simple process, the most plausible mechanism appears to us to be as follows:

$$HCN + H_2S \longrightarrow H.CS.NH_2$$

$$H.CS.NH_2 + HCN \longrightarrow NH{:}CH.CS.NH_2$$

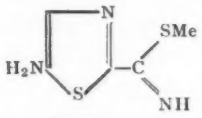
(VII)



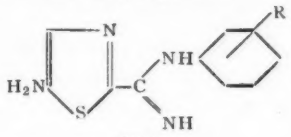
(VII) (VII) (II)

That thioformamide is an intermediate is certain because it itself with hydrogen cyanide furnishes chrysean. Since the compound (VII) should be very reactive it can not only condense with itself in which case chrysean is formed but can also polymerise. We do get, along with chrysean, a lot of tarry product, probably the polymerised product of (VII). This mechanism gives us a clue to devise new methods of synthesis of 5-aminothiazoles, which we are attempting.

On treatment with methyl iodide, chrysean easily furnishes the S-methyl derivative (VIII); under these conditions, the quaternary salt is not formed. The S-methyl derivative easily reacts with aromatic amines (aniline, *p*-chloraniline and *m*-aminophenol) to furnish the amidino derivatives (IX) which were prepared for testing their antimalarial properties.

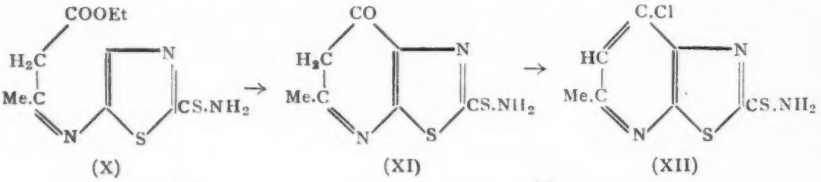


(VIII)

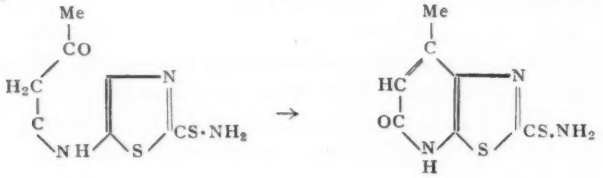


(IX)

The amino group of chrysean behaves as that of a typical aromatic amine. With the use of acetoacetic ester under the conditions of the Knorr-Conrad-Limpach synthesis, we could obtain a new type of pyridinothiazole. Chrysean with acetoacetic ester furnishes the acrylidene derivative (X) which on heating in Dowtherm for a short while easily cyclises to the pyridino-thiazole compound (XI); this with phosphorus oxychloride is converted into the chloro derivative (XII) wherein the chlorine atom is very reactive.



(X) (XI) (XII)



(XIII) (XIV)

On the other hand, the acetoacetyl derivative of chrysean (XIII) obtained by heating chrysean with acetoacetic ester at 145–50° C., does not cyclise on

heating with Dowtherm to the pyridinothiazole derivative (XIV). Attempts to effect the cyclisation with sulphuric acid caused decomposition. The properties of the pyridinothiazoles obtained are being studied.

Experimental

Chrysean.—A rapid stream of hydrogen sulphide was passed into a concentrated solution of sodium cyanide (200 g.) containing a little ammonia. Soon a golden yellow crystalline product separated. When there was no further increase in the separation of the crystalline product, it was filtered and washed (18 g.); m.p. 202–4°. In spite of numerous experiments we could not obtain a better yield of the product; this might be because the quality of the sodium cyanide we used was not quite good.

The above crystalline product was dissolved in boiling water and filtered. The crystals that separated on cooling were filtered off and a second crop was obtained by cooling the filtrate in ice-cold water. These were collected (m.p. 216–8°) and on crystallising once more from water, it separated in shining golden yellow plates (10–12 g.); m.p. 222° C. (Found: N, 26·02; $C_4H_5N_3S_2$ requires N, 26·4 per cent).

The mother liquor yielded a crop in needles (2–3 g.); m.p. 150–80°. On repeated crystallisation this was separated into the plates, m.p. 216–18° and the other fraction crystallising in needles, m.p. 146–46·5° (Found: N, 26·0; $C_4H_5N_3S_2$ requires N, 26·4 per cent.). On admixture of the two, the melting point was 170–80°.

The same type of fractionation could be carried out by using alcohol instead of water.

Both the forms yield the same acetamino compound, softening at 214° and melting with decomposition at 236–7° (Found: N, 20·61 ; $C_6H_7ON_3S_2$ requires N, 20·89 per cent.).

Both these forms on degradation according to the method of Hellsing furnished 5-acetamidothiazole.

S-Methylchrysean hydroiodide (VIII).—Chrysean (2 g.) was suspended in alcohol (10 c.c.), methyliodide (2·5 g.) added and the reaction mixture refluxed on the steam-bath for 10–15 minutes. The solution which was clear threw down immediately the hydroiodide of the S-methyl derivative. After cooling the crystalline mass was filtered (3·2 g.) and recrystallised from alcohol; m.p. 180° C. (Found: N, 13·6; $C_5H_7N_3S_2$, HI requires N, 13·9 per cent.).

5-*Amino*-2-(*N-phenylamidino*)-*thiazole.*—A mixture of the above described hydroiodide (2·2 g.), aniline (0·7 g.), and water (20 c.c.) was refluxed

for 10 hours when the smell of the evolving mercaptan ceased. The reaction mixture was cooled, filtered from the tarry mass and the filtrate made alkaline when a pasty mass separated. It became granular after two days (1·1 g.). It was filtered and on crystallisation from benzene, it separated in beautiful golden yellow needles, m.p. 148° C. (Found: N, 25·2; $C_{10}H_{10}N_4S$ requires N, 25·6 per cent.).

5-*Amino*-2-(*N*-p-*chlorophenyl*)-*amidinothiazole*.—This was prepared as above by using *p*-chloraniline in the place of aniline. The compound crystallised from benzene and had m.p. 144–5° (Found: N, 21·62; $C_{10}H_9N_4SCl$ requires N, 22·17 per cent.).

5-*Amino*-2-(*N-metahydroxyphenyl*)-*amidinothiazole*.—Prepared as above described by using *m*-aminophenol in the place of aniline. It crystallised from alcohol in golden yellow needles; m.p. 215–6° (Found: N, 23·80; $C_{10}H_{10}ON_4S$ requires N, 23·93 per cent.).

Acrylidene derivative (*X*).—A mixture of chrysean (4·0 g.), acetoacetic ester (3·5 g.) and alcohol (20 c.c.) was refluxed on the steam-bath for 6 hours, the alcohol removed by distillation under reduced pressure and the residue crystallised from alcohol whereby the condensation product separated in needles; m.p. 149° (yield, 3·0 g.) (Found: N, 15·2; $C_{10}H_{13}O_2N_3S_2$ requires N, 15·5 per cent.).

2-*Thioamido*-4-*hydroxy*-6-*methylpyridinothiazole* (*XI*).—The above condensation product (3·0 g.) in Dowtherm (15 c.c.) was heated to 250° C. and maintained there for 15 minutes when a dark brown solid was thrown out. It was cooled, filtered and washed (1·0 g.); being insoluble in all organic solvents it could not be crystallised.

2-*Thioamido*-4-*chloro*-6-*methylpyridinothiazole* (*XII*).—The foregoing compound (1·0 g.) was treated with phosphorus oxychloride (2·0 c.c.) with cooling. After the vigorous reaction subsided, the mixture was refluxed on the steam-bath for 15 minutes and then poured on ice. The solid that separated was collected and crystallised from alcohol (yield, 0·8 g.); m.p. 178–9° (Found: N, 17·3; $C_8H_6N_3S_2Cl$ requires N, 17·24 per cent.). This compound is easily desulphurised indicating the presence of the thioamide group. It also reacts with amines indicating that the chlorine atom is reactive.

Acetoacetylchrysean (*XIII*).—A mixture of chrysean (4·5 g.) and acetoacetic ester (20 c.c.) was heated in an oil-bath at 145–50° C. for 2 hours. The reaction mixture was cooled, the solid that had separated was filtered off (2·0 g.) and crystallised from alcohol; m.p. 208–10° (Found: N, 17·0; $C_8H_9O_2N_3S_2$ requires N, 17·2 per cent.).

We thank Mr. M. H. Shah, Microanalyst, for carrying out the analyses reported.

SUMMARY

Chrysean has been isolated in two forms; whether they are stereosoimers or only dimorphic forms is discussed. A mechanism of formation of chrysean is suggested. With methyl iodide it gives readily the S-methyl derivative which reacts easily with aniline, *p*-chloraniline and *m*-aminophenol to furnish the amidino derivatives of formula (IX). Chrysean on being refluxed with ethyl acetoacetate in alcohol gave the acrylidene derivative (X) which cyclises on heating to the pyridinothiazole derivative (XI). Ethyl acetoacetate and chrysean at higher temperature condensed to yield the acetoacetyl derivative (XIII) which however did not cyclise to furnish (XIV).

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ON WEBER'S DIFFERENTIAL EQUATION

By B. S. Popov

(Institute de Mathematiques Faculte de Philosophic, Skopje)

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THIS paper is concerned with the factorisation of a differential operator. We give the necessary and sufficient condition that a differential operator may be factored into simpler operators.

Consider the generalized Weber's differential equation*

$$\mathrm{L}(x, \mathrm{D}) \equiv y'' + \mathrm{P}_1 y' + \mathrm{P}_2 y = 0, \ \mathrm{D} = \frac{d}{dx} \tag{1}$$

where P_i are real polynomials of degree 1, 2 respectively, *i.e.*,

$$\mathrm{P}_i(x) = a_{i1}x^2 + a_{i2}x + a_{i3}; \ a_{11} = 0$$

a_{ik} are arbitrary constants.

If we assume that the operator $L(x, D)$ can be separated into two factors

$$\left(\mathrm{D} + f_1(x) + \frac{f_2'(x)}{f_2(x)}\right) \text{ and } \left(\mathrm{D} + \frac{f_3(x)}{f_2(x)}\right)$$

then the differential equation (1) may be written in the form

$$\mathrm{L}(x, \mathrm{D})\, y = \left[\mathrm{D} + f_1 + \frac{f_2'}{f_2}\right]\left[\mathrm{D} + \frac{f_3}{f_2}\right] y = 0 \tag{2}$$

In this case we have the identities {1}

$$\begin{aligned} f_2' + f_3 + f_1 f_2 - \mathrm{P}_1 f_2 &\equiv 0 \\ f_3' + f_1 f_3 - \mathrm{P}_2 f_2 &\equiv 0 \end{aligned} \tag{3}$$

Let the functions f_i be the polynomials of the form

$$f_i(x) = \sum_{k=0}^{n+1} \beta_{i,k} x^{n-k+1} \tag{4}$$

$$\beta_{1,k} = 0, \ k = 0, 1, \ldots . n-1, \ \beta_{2,0} = 0, \ \beta_{2,1} = 1$$

* The primes denote derivatives with respect to x.

Replacing $f_i(x)$ in (3) by its values from (4), we obtain the system of $2n+5$ non-linear algebraic equations

$$(n-k+2)\,\beta_{2,\,k-2}+(\beta_{1,\,n+1}-a_{13})\,\beta_{2,\,k-1}+(\beta_{1,\,n}-a_{22})\,\beta_{2,\,k}+\beta_{3,\,k}=0$$

$$(n-k+2)\,\beta_{3,\,k-1}+\beta_{1,\,n+1}\,\beta_{3,\,k}+\beta_{1,\,n}\,\beta_{3,\,k+1}-a_{21}\,\beta_{2,\,k+1}-a_{22}\,\beta_{2,\,k}$$
$$-a_{23}\,\beta_{2,\,k-1}=0,$$
$$(k=0,\,1,\,2,\ldots.n+2).$$

By solving these equations, we get the coefficients of the polynomials

$$\beta_{2,\,1}=\frac{(a_{12}\,a_{13}-2a_{22})\,n}{a_{12}^{\,2}-4a_{21}},\quad (k+1)\,\beta_{2,\,k+1}=\frac{n-k}{k}\,\beta_{2,\,1}\,\beta_{2,\,k}$$
$$\mp\frac{(n-k)\,(n-k+1)}{(a_{12}^{\,2}-4a_{21})^{\frac{1}{2}}}\,\beta_{2,\,k-1},$$

$$2\,\beta_{1,\,n}=a_{12}\mp(a_{12}^{\,2}-4a_{21})^{\frac{1}{2}},\quad 2n\,\beta_{1,\,n+1}=na_{13}\mp(a_{12}^{\,2}-4a_{21})^{\frac{1}{2}}\,\beta_{2,\,1},\quad (5)$$

$$2\,\beta_{3,\,0}=a_{12}\pm(a_{12}^{\,2}-4a_{21})^{\frac{1}{2}},$$

$$\beta_{3,\,k}=\beta_{3,\,0}\,\beta_{2,k}+\frac{na_{13}\pm\beta_{2,\,1}\,(a_{12}^{\,2}-4a_{21})^{\frac{1}{2}}}{2n}\,\beta_{2,\,k-1}-(n-k+2)\,\beta_{2,\,k-2},$$
$$(k=1,\,2,\ldots.n+1)$$

and the relation for the natural number n determining the degree of the polynomials

$$(a_{12}\,a_{13}-2a_{22})^2+(a_{12}^{\,2}-4a_{21})\,(4a_{23}-2a_{12}-a_{13}^{\,2})$$
$$=\pm\,2\,(2n+1)\,(a_{12}^{\,2}-4a_{21})^{3/2}.\quad (6)$$

The preceding relation must be satisfied for the coefficients a_{ik} such that $L(x, D)$ can be separated in the form (2). It is the necessary condition. It is easy to show, with respect to (1), that this condition is sufficient too.

Thus one obtains the following results:

The necessary and sufficient condition that the generalized Weber's equation (1) *may be written in the form* (2) *is that the relation* (6) *is satisfied.*

In this case the functions $f_i(x)$ are the polynomials (4), the coefficients of which are determined by (5).

It is obvious that we can solve completely the equation (1), if it can be written in the form (2). According to the relation (6) represents the *integrability condition* too.

For the special Weber's differential equation {2}

$$y'' = \tfrac{1}{4}(x^2 + a)\, y,$$

we have from (6) $a = \mp 2(2n + 1)$ and we obtain

$$\left[\mathrm{D} + \frac{\mathrm{H}_n'}{\mathrm{H}_n} - \frac{x}{2}\right]\left[\mathrm{D} + \frac{\mathrm{R}}{\mathrm{H}_n}\right] y = 0$$

where

$$\mathrm{R} = \tfrac{1}{2}x^{n+1} - \binom{n}{1}\frac{n+3}{4}x^{n-1} + 3\binom{n}{3}\frac{n+5}{8}x^{n-3}\ldots,$$

$$\mathrm{H}_n = \mathrm{He}_n(x) = (1)^n e^{x^2/2}\,\mathrm{D}(e^{-x^2/2}).$$

Differential equation {3}

$$\mathrm{Y}'' + x\mathrm{Y}' + (n+1)\,\mathrm{Y} = 0,$$

may be written in the form

$$\left[\mathrm{D} + n\frac{\mathrm{H}_{n-1}}{\mathrm{H}_n}\right]\left[\mathrm{D} + \frac{\mathrm{H}_{n+1}}{\mathrm{H}_n}\right]\mathrm{Y} = 0.$$

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SOME ILLUSTRATIONS OF THE THEORY OF THE CHRISTIANSEN OPTICAL FILTERS

By M. R. Bhat

(From the Raman Research Institute, Bangalore)

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(Communicated by Sir C. V. Raman)

1. Introduction

The functioning of the well-known Christiansen optical filters for obtaining an approximately monochromatic beam of light depends on the behaviour of an optically isotropic solid, *e.g.*, glass, when powdered and immersed in a flat-sided cell containing a liquid mixture of suitably adjusted refractive index. The principles of geometrical optics indicate that since the contents of the cell are optically heterogeneous, a pencil of white light entering the cell would suffer reflections and refractions at the boundaries between the solid and the liquid and would therefore fail to emerge in its original direction. An exception however arises when the refractive indices of the solid and the liquid in which it is immersed are identical for a particular wave-length in the spectrum. A beam of light having such wave-length would accordingly traverse the cell and emerge from it without any disturbance. Beams of other wave-lengths for which the refractive indices are unequal would be turned aside as already stated. It follows that the cell would function as a monochromatizer for the light transmitted through it.

The foregoing account of the principles on which a Christiansen filter works is based on the ideas of geometrical optics. That such an account is inadequate is shown by an observation made by Christiansen himself and described in his original paper (1884). He noticed that the regularly transmitted light when examined spectroscopically has a finite observable spectral width and that such width is notably influenced by the size of the particles of the solid powder. As the particle size is diminished, the band of transmission in the spectrum widens out, till finally with the smallest particles of all obtained by prolonged grinding and elutriation, practically the whole of the spectrum appears in the regularly transmitted light. Other factors besides the particle size also influence the observed behaviour of a Christiansen cell. Rayleigh (1899) noticed that the spectral width of the light transmitted by powdered glass immersed in a mixture of carbon disulphide and benzene increased fourfold when the thickness of the cell is diminished from

20 to 5 mm. He also found that the performance of the cell is influenced notably by the relation between the dispersive powers of the powder and the liquid. For instance, the spectral width of the regularly transmitted light increased threefold when the mixture of carbon disulphide and benzene was replaced by cedar-wood oil with a little of carbon disulphide added to it.

For a correct appreciation of the functioning of a Christiansen filter, it is necessary to approach the subject from the standpoint of the wave-theory of light. The operation of the filter clearly depends upon the relative retardations in phase of the different parts of the wave-front of light when it passes through the cell and traverses the media of different refractive indices. If the differences in phase arising in the passage of light through a single layer of particles are small enough in comparison with the wave-length of the light, the contents of the cell would behave as an optically homogeneous medium in spite of the difference in the refractive indices of the media contained in the cell. The shape and size of the particles of the solid powder, the fraction of the total volume which they occupy, the difference in the dispersive powers of the two media, the total thickness of the cell, and finally also the wave-length of the light determine the magnitude of the phase differences which arise and hence also the spectral character of the transmitted light. The energy which fails to appear in the transmitted light would naturally be found as diffracted radiation.

Basing himself partly on the results of his experimental observations and partly on theoretical considerations, N. K. Sethi (1920) suggested the following formula for the transmission coefficient of a Christiansen cell.

$$I_z = I_0 e^{-k\left(\frac{\mu_1 - \mu_2}{\lambda}\right)^2 \Delta \cdot Z}$$

where I_z is the intensity emerging from a cell of thickness Z containing particles of diameter Δ, for an intensity I_0 incident upon it, $(\mu_1 - \mu_2)$ is the difference in the refractive indices of the solid and liquid media for the wave-length λ, and k is an empirical constant. A formal derivation of Sethi's formula on purely theoretical grounds has been given by Sir C. V. Raman (1949) in these *Proceedings*, the constant k being now a quantity capable of being computed theoretically when the size, shape and the disposition of the particles in the cell are known. It should be remembered in this connection that in the derivation of the formula the particles are assumed to be much larger than the wave-length of light and therefore very far indeed from being of colloidal dimensions. The appearance of λ^{-2} instead of λ^{-4} in the exponential is therefore readily understood.

Very few of the accounts of the working of a Christiansen filter which have appeared in the literature make any reference to Sethi's fundamental contributions to the subject. In view of this, it has appeared desirable to publish in these *Proceedings* by way of a supplement to the theoretical paper of Sir C. V. Raman already mentioned, a series of spectrograms illustrating the dependance of the functioning of a Christiansen cell on the five factors mentioned above, *viz.*, the relative dispersive powers of the solid and the liquid, the wave-length of the light, the size of the particles, the thickness of the cell and the disposition of the particles within the cell, the latter including especially the proportion of the total volume of the cell occupied by the particles of the solid.

2. Spectral Character of the Transmitted Light

As was observed experimentally by Sethi and is also indicated by his formula, the curve of the distribution of intensity in the spectrum of the light transmitted by a Christiansen filter has a Gaussian form. It exhibits a peak of maximum intensity at the wave-length for which the powder and liquid have equal refractive indices, while on either side it falls off with the increasing difference in these indices. The sharpness of the peak of transmission is accordingly determined by the magnitude of the difference in the dispersive powers of the two media in the vicinity of the wave-length of maximum transmission. If this difference is small, the band of transmission may be expected to extend over a wide range of the spectrum, while, *per contra*, if the powder and liquid differ widely in their dispersive powers, the transmission band should be sharp. Strictly speaking, the width of the band is not a definable quantity unless we specify the fraction of the maximum intensity at its centre which is regarded as setting a limit to its extension on either side. The particular wave-length at which the powder and its surrounding liquid have identical indices can be shifted along the spectrum by the addition of an appropriately chosen second component to the liquid contained in the cell. The shift in the spectral position of the transmission band thus brought about should be accompanied by a notable sharpening of the band if the shift is towards the violet end of spectrum. For, the dispersive powers of transparent solids and liquids usually increase rapidly with diminution in the wave-length of the light, and hence the difference in the dispersive powers of the two media may normally be expected to behave likewise. Such sharpening of the transmission band accompanying its shift in position should, according to the Sethi formula, become more pronounced by reason of the diminishing value of λ which appears in the inverse square power in the exponential of the formula.

The role played by the difference in the dispersive powers of the powder and liquid filling its interstices on the optical behaviour of a Christiansen filter is most strikingly illustrated by choosing substances for which this difference is very small. A very convenient example is furnished by powdered KCl immersed in a cell containing sym-$C_2H_2Cl_4$ to which a few drops of CCl_4 have been added to equalise the indices of the powder and liquid for any chosen part of the spectrum.

TABLE I

Refractive Indices

Substance	$n_{G'}$ $\lambda = 4340{\cdot}6$	n_F $\lambda = 4861$	n_D $\lambda = 5893$	n_C $\lambda = 6563$	$n_{G'} - n_C$
CCl_4 (20° C.) ..	1·47290	1·46755	1·46072	1·45789	·01501
KCl (18° C.) ..	1·50493	1·49835	1·49036	1·48721	·01772
sym-$C_2H_2Cl_4$ (15° C.) ..	1·50954	1·50381	1·49678	1·49302	·01652

It will be seen from Table I that in the visible spectrum, KCl has a slightly lower index than sym-$C_2H_2Cl_4$ but a slightly higher dispersive power. The addition of a little CCl_4 brings the refractive indices of the powder and liquid into coincidence almost simultaneously throughout the whole spectrum. Actually, such coincidence first occurs at the violet end of the spectrum and then shifts towards the red. If the experiments are made with the material placed inside a flat cell, colours are indeed noticeable in the transmitted light, but they are not very vivid, while the halo of diffracted light seen surrounding the source exhibits hardly any chromatic effects. The great extension of the spectral band of transmission in the present case becomes directly evident to observation if the powder and liquid are placed together in a hollow glass prism of 60° angle and the straight bright filament of an electric lamp is viewed through the mixture. The filamentary source is then seen drawn out into a spectral band of considerable extension whose position alters with the quantity of CCl_4 present or with the temperature of the cell. On the other hand, if a similar experiment be made with materials exhibiting a large difference in the dispersive powers, *e.g.*, hexamethylene-tetramine powder immersed in a mixture of CS_2 and C_6H_6 in a flat cell, brilliant chromatic effects are observed in the transmitted light, and the complementary colours are seen in the diffraction halo; viewed through a hollow prism, the filament source is seen as a sharp monochromatic line.

A progressive narrowing of the spectral band of transmission occurs when powdered KCl is placed in a flat-sided cell and the same is filled up with one or other of a series of liquid mixtures the principal component of which has a higher dispersive power than KCl in ascending sequence. Tetrachloroethylene (C_2Cl_4), xylene, toluene, benzene and carbon disulphide from such a series. As the refractive indices of these liquids are also greater than those of KCl, the addition of a second component of lower index is necessary to obtain a transmission band in the visible spectrum. Carbon tetrachloride is suitable for this purpose in the case of the first four liquids of the series, while acetone is a more suitable diluent for CS_2. The addition of the second component diminishes the dispersive power of the mixture, but it nevertheless remains higher than that of KCl. The residual difference is small when C_2Cl_4 is the principal component, larger with xylene, and quite large for the CS_2-acetone mixture. The progressive sharpening of the band of transmission is illustrated in Figs. 1, 2 and 3 (Plate I) for these three cases respectively. Each figure exhibits a set of spectra in which the position of the transmission band had been shifted towards the violet by graduated additions of the second component. It will be seen that very broad transmission bands appear in Fig. 1, and that they are much sharper in Fig. 2 and quite sharp in Fig. 3. Each series of spectra also indicates the notable sharpening of the bands when they are shifted towards the violet by additions of the second component. Such sharpening is actually more striking than might seem at first sight, since the dispersive power of the spectrograph employed increases greatly towards the shorter wave-lengths. A comparison with the wave-length scale recorded in the pictures enables the situation to be better appreciated. It should be mentioned that the spectrograms reproduced in Plate I were obtained by focussing the image of a narrow slit illuminated by an electric arc on the slit of the instrument itself, the Christiansen cell being placed immediately in front of the focussing lens.

A notable feature in all the three sets of spectrograms reproduced in the Plate is that the transmission band is accompanied by a faint continuous spectrum extending unsymmetrically on either side of it. Such extension can be traced right up to the limit of the sensitivity of the photographic plate at the red end of the spectrum, whereas it falls off very quickly towards the violet. It does not appear likely that this feature is due to an admixture of the light regularly transmitted by the cell with the light diffracted in other directions. For, the optical arrangements described above were designed to prevent such an admixture. It would seem rather that the feature referred to is characteristic of the Christiansen effect itself. Indeed, one could have anticipated it from the Sethi formula, since the expression appearing as

the exponential in the formula increases much more slowly with increasing than with diminishing wave-lengths.

3. INFLUENCE OF PARTICLE SIZE

The dependence of the spectral width of the transmitted light on the size of the particles of the powder is illustrated in the series of spectra reproduced in Figs. 4, 5 and 6, Plate II. These spectrograms were obtained with glass powder immersed in a flat cell containing a mixture of CS_2 and C_6H_6. The thickness of the cell in all the cases was the same, *viz.*, 3 mm., but the particle sizes however were very different. The series of spectrograms in Fig. 4 were taken with particles of an average dimension of 9μ, obtained by prolonged grinding and elutriation of the powdered material with water. The spectrograms reproduced in Fig. 5 were obtained with particles of larger size averaging 100μ, and those in Fig. 6 with particles still larger in size, *viz.*, 270μ. These three sets of spectra strikingly exhibit the broadening of transmission band with diminishing particle size indicated by theory. The six spectra in each set exhibit the effect of successive increases of the proportion of C_6H_6 in its mixture with CS_2. The notable sharpening of the band thus resulting will be evident on a reference to the wave-length scale reproduced with the spectra.

Figs. 7 and 8, Plate III similarly illustrate the effect of increasing the thickness of the Christiansen filter. The spectra reproduced in it were recorded with powdered glass of the same average particle size, *viz.*, 100μ in both cases, but with two different thicknesses of the cell, *viz.*, 3 mm. in Fig. 7 and 10 mm. in Fig. 8. It will be noticed that the wave-length range of transmission is reduced roughly in inverse proportion to the thickness of the cell employed. These spectrograms likewise illustrate the very great spectral sharpening when the transmission band is shifted towards the violet end of the spectrum by additional quantities of the second component in the liquid mixture.

It should be mentioned in this connection that the influence of the thickness of the transmitting layer in the Christiansen experiment can be very well demonstrated by using a hollow prism instead of a flat cell and viewing a bright linear source of light with the eye placed close to the second surface of the prism. As the observer moves his eye along the surface of the prism from the edge towards the base, the image of the source seen through the prism and drawn out into a spectrum rapidly sharpens into a monochromatic band of very small width.

4. INFLUENCE OF LOOSE PACKING

The spectrograms reproduced in Figs. 1 to 8 in Plates I, II and III were recorded when the solid powder in the Christiansen cell had settled down

completely and hence the liquid occupied only the interstices between the solid particles. In such a case the powder is rather closely packed, and the volume occupied by it exceeds that of the liquid. A more open order of distribution of the solid particles in which the volume occupied by the liquid is comparable with or in excess of that occupied by the solid can be obtained as follows. The materials placed in the Christiansen cell are so chosen that the solid and the liquid mixture do not differ greatly in density, *viz.*, hexamine powder and a CS_2–C_6H_6 mixture. An excess of the liquid is put into the cell and a suitable quantity of the powder is distributed uniformly through its volume by vigorously shaking the cell. The powder remains suspended in the liquid for an appreciable time, since the densities of the two media are not different. As the powder settles down slowly, the quantity of the solid in the upper portion of the liquid column decreases gradually and the packing of the solid particles becomes increasingly less dense in this part of the liquid. Such a change should be accompanied by a gradual broadening of the spectral width of transmission through this part of the cell. For, it follows from the theoretical considerations leading to the Sethi formula that the constant k diminishes as the quantity of powder in suspension in the liquid is reduced, ultimately tending to zero when the liquid is nearly free of all the suspended material. The successive stages of the increase in the spectral width of transmission can be readily observed by employing a hollow prism as the container, as mentioned above. In the initial stages, when all the solid in the cell is suspended in the liquid, the image of the source appears as almost perfectly monochromatic when viewed through the prism. As more and more of the powder settles down, the image spreads out and finally extends over the whole spectrum. These changes can be recorded as follows. Light emerging from a narrow illuminated slit passes through the upper part of a column of the mixture contained in a flat cell and is focussed on the slit of a spectrograph. The cell is at first vigorously shaken and the transmission spectrum is recorded at successive short intervals of time as the powder settles down slowly. Such a series of spectrograms is reproduced in Fig. 9 in Plate IV and exhibits conspicuously the progressive widening of the spectral region of transmission. It is interesting to note the pronounced asymmetry in the distribution of intensity in the spectrum. In the final stages of the experiment, only very fine particles will remain suspended in the liquid. Their small size would naturally tend to enhance to a certain extent the width of the spectral band of transmission resulting from loose packing of the solid. Hence we have to bear in mind that the observed spectral character of the transmitted light is determined by the joint effect of these two factors, and not by the looseness of the packing alone.

5. THE CASE OF VERY LARGE PARTICLES

The Sethi formula indicates that the light transmitted by a Christiansen cell would have a continuous spectral distribution of intensity. It is not difficult to understand why such a result is reached despite the assumptions made in deriving the formula, *viz.*, that the particles in the cell are approximately uniform in size and are not small in comparison with the wave-length of light. In the first place, it is assumed that each of the successive layers into which the contents of the cell can be conceived to be divided contains a great number of particles. It is assumed further that the cell contains a great number of such layers acting independently. As a consequence of these assumptions, the fluctuations of intensity with wave-length which would be exhibited in the light diffracted by a single particle are completely smoothed-out when the integrated effects of all of them acting together are evaluated. If, however, the particles contained in the cell are very large and the total thickness of the cell is sufficient to include only a few layers of such particles, it is not to be expected that a smoothed-out distribution of intensity would be observed in the spectrum of the transmitted light. Fluctuations of intensity dependent on the size of the particles as well as their number and arrangement in the cell may be expected to be observed. Effects of the kind indicated above have actually been observed in the transmission spectrum of a Christiansen cell containing particles of diameter of 1, 2 and 3 mm. respectively in a cell 10 mm. thick filled with a CS_2-acetone mixture. A group of spectrograms of the transmitted light in the particular case of particles of average size 3 mm. as recorded with increasing exposures is reproduced in Fig. 10, Plate IV. With small exposures, only the most intense part of the transmitted light is recorded. This is found to extend over a very narrow range of wave-lengths as is to be expected from the Sethi formula. In the succeeding spectrograms taken with increasing exposures, the transmission spectrum is found to broaden out asymmetrically, showing less extension towards the violet end of the spectrum. This of course is due to the more rapid increase of the difference in the dispersive powers of the solid and liquid media on the violet side of the maximum of transmission than on the red side. These spectrograms clearly exhibit quasi-periodic fluctuations in the spectral distribution of the transmitted light. In the first few spectrograms, close to the most intense part of the transmission we can detect a series of maxima and minima of intensity. Observations with particles respectively of 1, 2 and 3 mm. diameter show that the spacing of these bands varies inversely with the particle size. Such a result is to be expected from theoretical considerations based on wave-optical principles.

6. Spectral Character of the Diffracted Light

The first spectrogram in the group of spectra reproduced in Fig. 11, Plate IV is of the light transmitted by particles of glass of average size 270μ contained in a cell 10 mm. thick filled with a mixture of CS_2 and acetone. The succeeding spectrograms show the changes observed in the spectral character of the diffracted light as the direction of observation becomes increasingly inclined to the direction of the incident light. It will be seen that the spectrum consists of a central dark band flanked on either side by two bright bands. Both the dark and the bright bands are found to broaden out with increasing obliquity of observation. But the bright band on the side of greater wave-lengths ultimately extends to the very limit of the sensitivity of the plate, while on the side of the shorter wave-lengths the extension is comparatively little. Essentially similar observations were made by Sethi and are to be found illustrated in his paper. He also correlated these spectral characteristics of the diffracted light with the colours observed in the halo in different directions.

To understand the spectral character of the diffracted light in different directions, we have to take note of the following points. In the first place, the transmitted and diffracted radiations should exhibit complementary effects; the more freely light of a given wave-length is transmitted through the cell, the less would be the fraction of the same appearing as diffracted light. Secondly, we have to consider the distribution of the diffracted radiation in different directions. As was noticed by Sethi, the angular spread of the diffracted light is least for wave-lengths in the vicinity of that most freely transmitted and increases progressively as the wave-length is altered in either direction, the more so towards shorter wave-lengths since the phase differences arising from the passage of light through the particles of the powder are largest in that case. Such increase in the angular spread of the diffracted light is necessarily accompanied by a fall of its intensity as observed in particular directions. In each case, there is fairly a well-defined angle beyond which the intensity of the diffracted light becomes negligible. Taking these factors into account, the features observed in the spectrograms reproduced in Fig. 11, Plate IV are readily intelligible.

In conclusion, I wish to express my grateful thanks to Prof. Sir C. V. Raman for suggesting the problem and his guidance in the course of the work.

Summary

Studies of the spectral character of the light transmitted by Christiansen filters in various circumstances have been carried out and are discussed in

the light of wave-optical theory. The results are illustrated by a series of spectrograms reproduced with the paper. When the dispersive powers of the solid powder and of the liquid in which it is immersed are nearly equal, the transmission extends over a wide range of the spectrum. *Per contra*, it narrows down with increasing difference in the dispersive powers. The influence of the same factor is also strikingly evident when the wave-length of maximum transmission is shifted towards shorter wave-lengths by changing the composition of the liquid. A pronounced asymmetry is also noticeable in the spectral distribution of intensity of the transmitted light. The size of the particles of the powder and the total thickness of the filter are other factors which influence the spectral range of transmission. Of particular interest are the results obtained when the powder is only loosely suspended in the liquid and not tightly packed.

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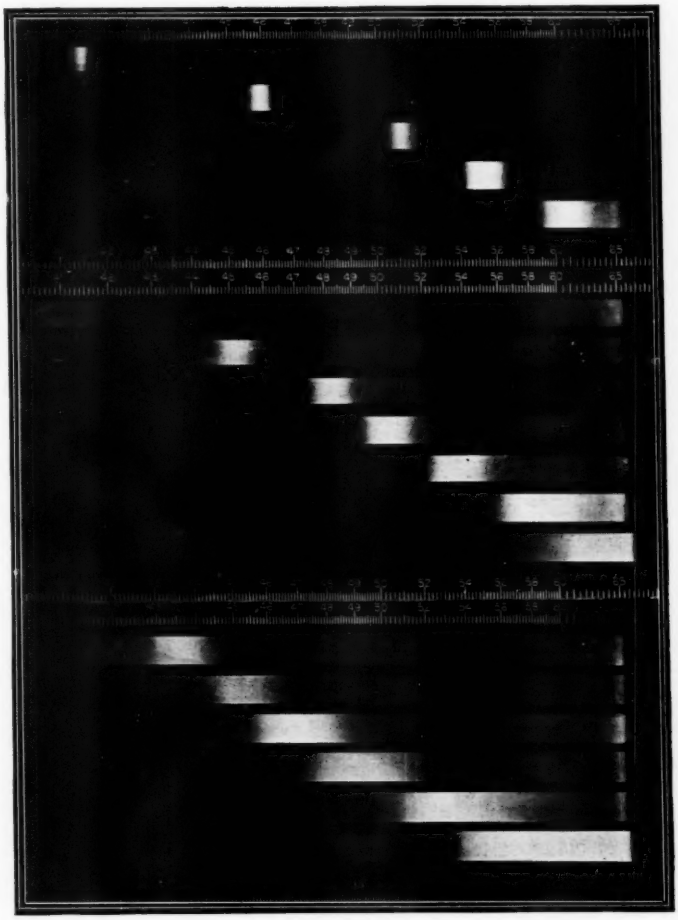

FIG. 3

FIG. 2

FIG. 1

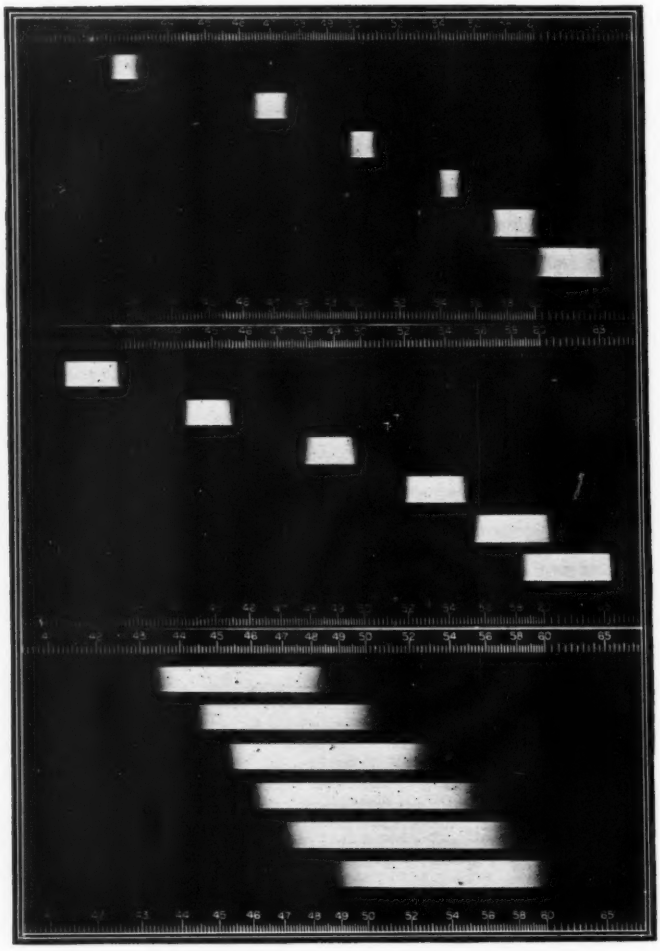

FIG. 6

FIG. 5

FIG. 4

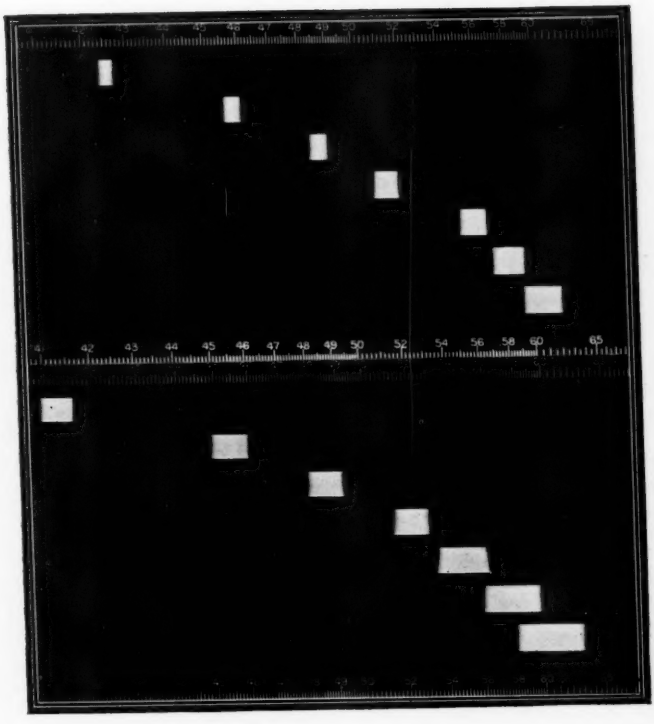

FIG. 8

FIG. 7

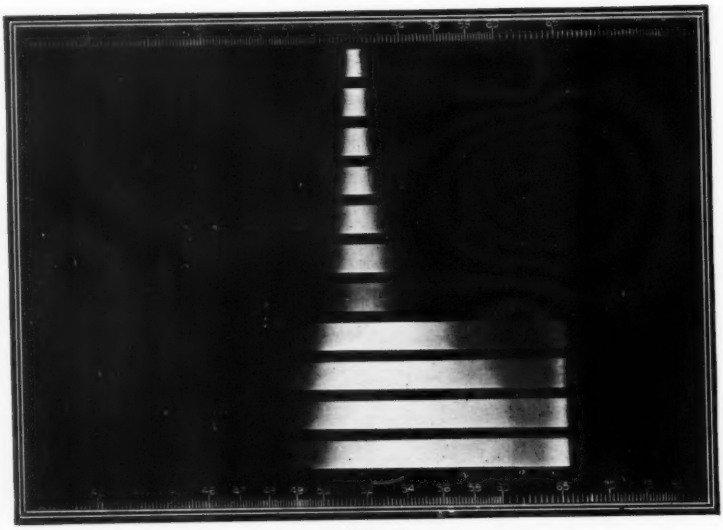

FIG. 9

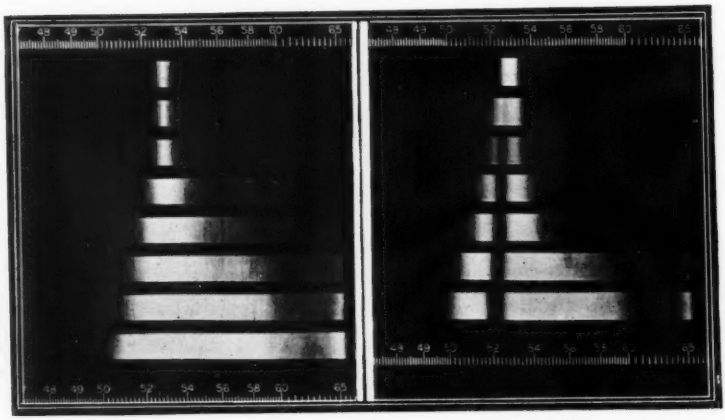

FIG. 10

FIG. 11

NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XLV. A Synthesis of Carajuridin Chloride and Carajurin

BY (MISS) L. PONNIAH AND T. R. SESHADRI, F.A.SC.
(From the Department of Chemistry, University of Delhi, Delhi)

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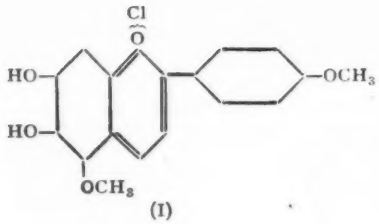
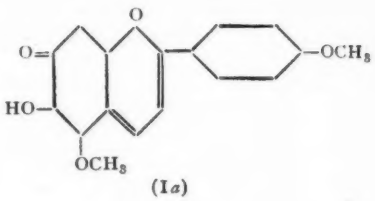
IN Part XLII of this series,[1] an account was given of exploratory work intended to lead to the synthesis of carajuridin chloride. In the course of this preliminary investigation, the preparation of polyhydroxy benzaldehydes using the method of nuclear oxidation with potassium persulphate was studied, a number of 6-hydroxy pyrylium salts of the gesneridin type were made and their properties recorded. The synthesis of carajuridin chloride itself has now been accomplished and forms the subject-matter of the present communication.

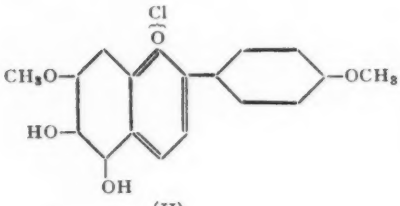
Carajura is the name of a rare cosmetic pigment used by the natives of the Orinoco. This was investigated by Chapman, Perkin and Robinson[2] who found that the main constituent is carajurin, the colour base of carajuridin. Carajurin had the molecular formula $C_{17}H_{14}O_5$ and readily formed the corresponding pyrylium salt, carajuridin chloride $C_{17}H_{15}O_5Cl$. Unlike the other naturally occurring anthocyanidins, carajuridin exhibited no tendency to pass into a pseudobase and hence was considered to have no hydroxyl in the 3-position. It was found to contain two methoxyl groups and yield *p*-acetoxy anisole when boiled with concentrated aqueous alkali and *p*-hydroxy benzoic acid on fusion with caustic potash; but no other identifiable product was obtained. On demethylation, it gave a tetrahydroxy flavylium chloride which was identified as scutellareinidin chloride (III) and which could be synthesised by the condensation of antiarol aldehyde and *p*-methoxy acetophenone and subsequent demethylation. The fact that *p*-acetoxy anisole was produced on boiling carajurin with aqueous concentrated alkali indicated that one of the methoxyl groups was situated in the 4′-position of the side-phenyl nucleus. Carajurin gave a brown-violet colour with ferric chloride indicating the presence of vicinal hydroxyl groups in the molecule. The constitutional formula for carajuridin chloride could therefore be either (I) or (II). Structure (II) would give rise to a violet or blue colour base and would be characterised by instability whereas structure (I) would form a stable red colour base. Hence the constitution for carajuridin was represented by (I) and the colour base carajurin by (I *a*).



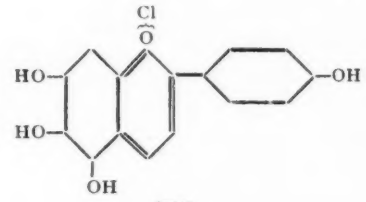
(I)



(Ia)

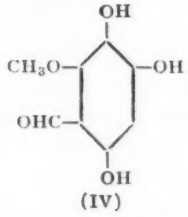


(II)

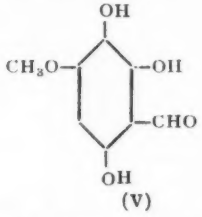


(III)

Vasey and Robinson[3] attempted to synthesise 2:4:5-trihydroxy-6-methoxy benzaldehyde (IV) which on condensation with *p*-methoxy acetophenone should yield carajuridin. They subjected 1:2:5-trihydroxy-3-methoxy benzene to the Gattermann condensation and instead of the expected aldehyde (IV), obtained a different product which condensed with *p*-methoxy acetophenone to form a flavylium salt which did not give any colour with ferric chloride. Hence it was concluded that the aldehyde was 2:3:6-trihydroxy-4-methoxy benzaldehyde, represented by formula (V) and the ring closure involved the 2-hydroxyl and not the 6-hydroxyl. Hence the synthesis of carajuridin could not be accomplished.



(IV)



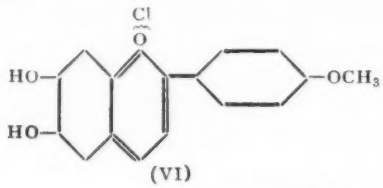
(V)

For carrying out an unambiguous synthesis of 5:4'-dimethoxy-6:7-dihydroxy flavylium chloride, 6-O-methyl phloroglucinaldehyde has now been used as the starting material and it has been prepared from monomethyl phloroglucinol.

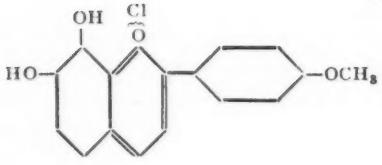
Herzig and Wenzel[4] subjected O-monomethyl phloroglucinol to the Gattermann condensation. They reported the formation of an aldehyde (m.p. 170°) which was considered to be 4-O-methyl phloroglucinaldehyde.

Karrer and Bloch[5] obtained two isomers (m.p. 203° and m.p. 139–40°) by partial methylation of phloroglucinaldehyde with diazomethane and separated them by fractional crystallisation from benzene. They studied their constitutions and showed that the higher melting substance was the 6-methyl ether and the lower melting one the 4-methyl ether. Leon, Robertson, Robinson and Seshadri[6] obtained 6-O-methyl phloroglucinaldehyde by methylation of 2:4-dibenzoyl phloroglucinaldehyde and subsequent debenzoylation. The same product melting at 208° was also prepared by them from monomethyl phloroglucinol by the Gattermann condensation. However in this reaction, the formation of small amounts of 4-O-methyl phloroglucinaldehyde is unavoidable and cannot be ignored. The resulting product which melts at about 170° is best purified by repeated fractional crystallisation from water containing sulphur dioxide. The pure sample (m.p. 208°) of 6-O-methyl phloroglucinaldehyde thus obtained is subjected to nuclear oxidation with potassium persulphate when 2:4:5-trihydroxy-6-methoxy benzaldehyde is produced. In its properties it closely resembles hydroxy quinol aldehyde. When condensed with *p*-methoxy acetophenone in glacial acetic acid medium at 25°, carajuridin chloride is obtained. The synthetic sample has been compared and found to be identical with a natural sample of carajuridin chloride kindly provided by Professor Sir Robert Robinson. The details of the comparison are given in the experimental part. Particular mention may be made of the capacity of carajuridin chloride to stain the skin a brilliant red shade. This property is also possessed by the simpler analogue, 6:7-dihydroxy-4′-methoxy flavylium chloride (VI) described in an earlier paper[1] which gives also most of the colour reactions exhibited by carajuridin. In contrast to this 7:8-dihydroxy-4′-methoxy flavylium chloride (VII) prepared according to the method of Robinson and Vasey[3] shows marked difference. It gives with ferric chloride a brilliant emerald green colour, forms a deep bluish purple colour base on treatment with sodium acetate and does not stain the skin. This marked difference is of some significance, since it definitely eliminates a further possibility for the constitution of carajuridin. It may be pointed out that the production of carajuretin (III) by the demethylation of carajuridin with hydriodic acid is an important consideration on which the constitution of carajurin is based. In the case of flavones, the possibility of 5:7:8-trihydroxy compounds undergoing change into 5:6:7-trihydroxy isomers during demethylation with hydriodic acid has been definitely established.[7] Though no experimental data are available in regard to the related flavylium salts, the possibility of this isomeric change could be visualised and carajuridin could then have the possible structure of 5:4′-dimethoxy-7:8-dihydroxy flavylium chloride

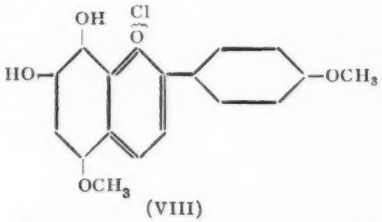
(VIII). The abovementioned ferric reaction of 7: 8-dihydroxy-4′-methoxy flavylium chloride rules out this possibility.



(VI)



(VII)



(VIII)

Another point that should be relevantly noted here is the wide range of colour of the ferric reaction encountered in the study of anthocyanidins. In the case of the commonly occurring anthocyanidins which are structurally related to flavonols and have *o*-dihydroxy groups only in the side phenyl nucleus, a positive ferric reaction is a blue colour. But this is different with the flavone analogue carajuridin which has *o*-dihydroxy groups in the 6: 7-positions of the condensed benzene ring and the positive reaction here is a purple colour; with the 7 : 8 disposition of the ortho hydroxy groups, this colour changes to emerald green.

EXPERIMENTAL

For the preparation of monomethyl phloroglucinol, the method of Robertson and Subramanian[9] has been employed with small modifications. Saturation of the methyl alcoholic solution of phloroglucinol with hydrogen chloride leads to the formation of dimethyl phloroglucinol mostly. Hence hydrogen chloride was passed at a slower rate (approximately 200 bubbles per minute) keeping the temperature between 20° and 25°. The methyl alcohol employed should also be quite pure. Even with these precautions, yields of the monomethyl ether were never consistent and varied according to the extent of saturation, though the total yield of the two ethers (mono and dimethyl ethers) was usually high.

2: 4-*Dihydroxy*-6-*methoxy benzaldehyde*

The product (7·5 g.) of the Gattermann condensation of monomethyl phloroglucinol using hydrogen cyanide was subjected to repeated fractional

crystallisation from water containing sulphur dioxide. After six crystallisations, the more sparingly soluble part consisting of 6-O-methyl phloroglucinaldehyde (2·2 g.) melted with decomposition at 208–10° with sintering at 202°.

2:4:5-*Trihydroxy-6-methoxy benzaldehyde* (*IV*)

6-O-Methyl phloroglucinaldehyde (2·2 g.) was dissolved in aqueous potassium hydroxide (3·75 g. in 38 c.c. of water) and the solution cooled to 10°. Potassium persulphate solution (3·6 g. in 100 c.c. of water) was added dropwise, in the course of 2 hours, while the mixture was kept continuously stirred. It was allowed to stand for 2 days at room temperature and then acidified to congo red and finally extracted repeatedly with ether to remove all the unchanged monomethyl phloroglucinaldehyde. To the aqueous solution, concentrated hydrochloric acid (60 c.c.) was added and the mixture was heated in a water-bath at 80° for 30 minutes. It was then cooled and extracted with ether. The ether solution was dried over sodium sulphate and the solvent distilled off. A dark viscous oil (about 200 mg.) was left behind, which could not be conveniently crystallised on account of its instability. However, it readily formed its 2:4-dinitro-phenylhydrazone which when crystallised twice from ethyl alcohol and once from ethyl acetate formed clusters of prismatic needles melting at 228–29° (Found: C, 46·1; H, 3·6; $C_{14}H_{12}O_8N_4$ requires C, 46·2; H, 3·3%).

Carajuridin chloride (*I*)

2:4:5-Trihydroxy-6-methoxy benzaldehyde (about 200 mg.) and *p*-methoxy acetophenone (300 mg.) were dissolved in glacial acetic acid (50 c.c.) and the solution saturated with dry hydrogen chloride at room temperature (25°). It was allowed to stand at room temperature for two days, excess of ether added and the precipitated pyrylium chloride filtered off. When allowed to stand in contact with a small amount of 1% hydrochloric acid, it became a definite crystalline looking solid (200 mg.). It was then extracted with hot 1% hydrochloric acid and the concentration of acid in the solution gradually raised to about 5% by adding concentrated hydrochloric acid. The portion that separated out during this process was not pure and hence filtered off. Hydrogen chloride gas was then passed into the filtrate till the solution became slightly turbid. On standing, it deposited glistening purplish red crystals of carajuridin chloride (25 mg.). On slow heating it softened at 129° and melted with decomposition at 202–04° (Found in air-dried sample: C, 54·9; H, 5·5; $C_{17}H_{15}O_5Cl$, $2H_2O$ requires C, 55·1; H, 5·1%. Found in a sample dried *in vacuo* at 80° for 6 hours: C, 61·2; H, 4·7; $C_{17}H_{15}O_5Cl$ requires C, 61·0; H, 4·5%). Under the microscope, both synthetic as well as natural carajuridin appeared as clusters

of prismatic needles. The synthetic sample consisting of bigger crystals was darker in colour, but when allowed to crystallise rapidly on the microscope slide from ethyl alcoholic hydrochloric acid, both synthetic as well as natural carajuridin appeared in the form of deep red leaflets. They dissolved in 1% hydrochloric acid to form identically coloured orange yellow solutions. A solution of the chloride in ethyl alcohol (orange) gives a dark brown colour on the addition of a drop of ferric chloride. The ferric reaction is best carried out following the procedure of Robinson and Robinson[8] for flower extracts. A dilute solution of carajuridin in 1% hydrochloric acid (golden yellow) was shaken well with amyl alcohol which extracts the pigment largely, forming an orange solution. Addition of sodium acetate renders amyl alcoholic solution deep crimson and the aqueous layer colourless. Ferric chloride changes the crimson colour to deep purple which is stable for several hours; excess of reagent does not make any change. The synthetic sample and the natural sample behaved similarly in the above treatment. Complete extraction with amyl alcohol from 1% hydrochloric acid has been considered to be characteristic of anthocyanidins. It is true in the case of anthocyanidins of the flavonol type, *e.g.*, peonidin. But carajuridin as well as other flavylium salts of the flavone type undergo incomplete extraction, although it is quite high. The aqueous layer definitely retains a small part of the salt.

In circular filter-paper chromatography,[10] using as solvent the aqueous phase of butanol-acetic acid-water mixture synthetic and natural carajuridin gave the same R_F value 0·60 at 29°. In a mixed chromatogram using two spots side by side a single ring was obtained confirming identity.

The absorption spectra of dilute solutions of synthetic as well as natural carajuridin have been studied using Beckmann spectrophotometer in the visible region; they are found to be identical, the absorption maxima being at 460 $m\mu$. From solutions in 1% hydrochloric acid both samples are easily extracted almost completely by the cyanidin reagent. They cause identical shades of a red stain on the skin.

Carajurin (*I a*)

Carajuridin chloride (5 mg.) was boiled with water (50 c.c.) for 2 hours under a layer of boiling benzene (50 c.c.). The benzene layer was then separated, dried over sodium sulphate and concentrated when brownish red prisms of carajurin were obtained (m.p. 180-85°). It was again dissolved in a small quantity of benzene (20 c.c.) and an equal volume of petroleum ether was added; the solution deposited on standing a brownish red crystalline solid which was filtered off and washed with a little benzene when pure

carajurin was obtained as garnet coloured prisms. It melted with decomposition at 200°. (The natural sample sintered at 200° and melted with decomposition at 202–04°; admixture with the synthetic sample did not depress the melting point.) Its alcoholic solution was orange in colour and gave a brown-violet colour with a drop of ferric chloride and it turned deep brown with excess of the reagent. The violet colour was more prominent when amyl alcohol was used. It was sparingly soluble in aqueous sodium hydroxide forming an orange red solution. In all these reactions the natural sample behaved quite similarly. When treated with alcoholic lead acetate, both synthetic and natural carajurin formed crimson coloured solutions which slowly deposited red needles. In circular filter-paper chromatography, using as solvent the aqueous phase of butanol-acetic acid-water mixture, both gave the same R_F value 0·56 at 29°.

Summary

The synthesis of carajuridin chloride and carajurin has been carried out starting with 6-O-methyl phloroglucinaldehyde, preparing 2:4:5-trihydroxy-6-methoxy benzaldehyde as an intermediate and condensing the latter with *p*-methoxy acetophenone. Identity with the natural products has been established by direct comparison using melting points, chromatography and colour reactions. This synthesis confirms the constitution proposed by Chapman, Perkin and Robinson for carajurin. 6:7-Dihydroxy-4′-methoxy flavylium chloride exhibits colour reactions very similar to carajuridin and the isomeric 7:8-dihydroxy-4′-methoxy flavylium chloride possesses very different properties thus excluding other possibilities for the constitution of carajuridin.

Our thanks are due to Professor Sir Robert Robinson for a supply of natural carajurin and carajuridin chloride which has enabled us to make direct and full comparison with the synthetic samples.

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STUDIES ON SOUTH INDIAN RADIOACTIVE MINERALS

Part I. Samarskite from Nellore

By U. Aswathanarayana, M.Sc.

(Department of Geology, Andhra University, Waltair)

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Abstract

Samarskite, a radioactive niobotantalate occurring in the Nellore pegmatites, has been studied in detail. The investigations comprise the determination of physical and optical characters, chemical composition, autoradiographic studies, distribution pattern, calculation and interpretation of age. The available data on Nellore Samarskite has been critically examined and it has been shown that the controversy raised by Holmes concerning the age of the Eastern Ghats can be solved, if the samarskite specimen analysed by Sarkar and Sen Sarma is understood to belong to the Gaya group of minerals, as has been later suggested. A tentative Archæan succession table has also been suggested.

Introduction

Samarskite, occurring as it does in the pegmatites intrusive into the Nellore schists, is of unique importance in the determination of the age of the Eastern Ghats and ultimately in the solution of Archæan Correlation problems like the continuity of Eastern Ghats and its relationship with Satpuras, the contemporaneity or otherwise of Nellore schists with the Dharwarian schists of Mysore, etc.

Previous Literature

The literature on Nellore samarskite may be broadly divided into two parts: (i) which treats samarskite as a chemical entity and deals with its nature of association, physical and optical characters, chemical composition formulæ, etc., and (ii) which utilises this data for geochronological studies. Bain,[1] Ellsworth,[2] Goldschmidt,[5] Karunakaran and Neelakantam,[8, 9, 10] Nandi and Sen,[14] Palache *et al.*,[15] Sarkar and Sen Sarma,[16] Yagoda,[17] have contributed to the first part of the studies and Holmes[16, 17] and Fermor[4] to the second part.

Experimental and Results

As the specific gravity is an index of the purity of the mineral, two determinations were made on two chips of the mineral. The lustrous fragment has a specific gravity of 5·75 and another chip with a coating of ochery material 5·36. Unaltered fragments have a lustrous velvet black colour, the lustre decreasing with alteration. Streak is brown with reddish tinge but when intergrown with non-radioactive columbate-tantalates develops a decided steel-grey tinge. Fracture is conchoidal.

Optical Characters

It is opaque even in thinnest slices. There is not even a faintest suggestion of its orthorhombic character. It is brown in reflected light.

Chemical Composition

Initially, the sample is broken into bits and the lustrous fragments are separated by hand-picking. They are then cleaned with a weak solution of nitric acid, washed repeatedly with distilled water, dried and powdered.

The mineral is chemically analysed by the well-known methods of Schoeller and Powell[17] and A. F. Williams.[18] The methods used in the estimation of rarer elements and lead are briefly described below:

1. *Columbium and Tantalum.*—The mineral is fused with potassium bisulphate and leached with tartaric acid solution. The earth acids are precipitated with tannin and finally ignited as $(Cb, Ta)_2O_5$.

2. *Uranium.*—The mineral is fused with bisulphate and leached with cold dilute hydrochloric acid. After a series of extractions, a chloride solution of U rare earths and aluminium is obtained. The rare earths are got rid of by double oxalate precipitation and alumina by double ammonium carbonate precipitation. Finally U is weighed as U_3O_8.

3. *Thorium.*—The mineral is fused with KOH and treated with dilute hydrochloric acid. The rare earths and thorium are separated by double oxalate precipitation and finally thorium is isolated from rare earths by precipitation with potassium iodate, converted into oxalate, ignited and weighed as ThO_2.

4. *Cerium and Yttrium earths.*—The rare earths are precipitated as oxalates in the hydrochloric acid medium. A broad separation between Ce and Yt earths is effected by double sulphate precipitation. Cerium is separated from Ce-earths by potassium iodate procedure.

5. *Lead.*—It is determined by the procedure evolved by Nandi and Sen.[14] The mineral is decomposed with hydrochloric acid and repeatedly

evaporated to dryness. Lead is precipitated as sulphide in the hydrochloric acid medium, converted to sulphate and extracted with ammonium acetate. The soluble lead acetate is converted into sulphate and weighed as such.

The values for the various constituents are recorded here, along with those given by other workers for Nellore samarskite (Table I).

TABLE I

	I	II	III	IV
Nb_2O_5 + Ta_2O_5 ..	56·29	52·57	57·40	58·65
TiO_2 ..	0·37	1·62	..	
SiO_2 ..	..	0·22	..	0·60
SnO_2 ..	..	1·48	..	0·50
FeO ..	9·30	14·77*	9·10	12·40*
CaO ..	1·41	0·94	1·10	1·03
MgO ..	..	0·03	..	0·75
Al_2O_3 ..	0·34	0·79	..	0·62
ThO_2 ..	1·32	1·21	1·98	1·33
Ce_2O_3† ..	1·51	0·81	1·20	1·54
Y_2O_3† ..	17·30	13·93	16·90	14·16
MnO ..	0·22	1·60	..	0·34
PbO ..	2·16‡	2·04	2·25	0·58
UO_2 ..	8·68	6·93	8·40	4·62
Na_2O+K_2O ..	0·26	0·50	..	..
Loss on ignition ..	0·63	0·29	0·87	1·12
	99·79	99·73	99·20	98·24

* Fe_2O_3.
† Uncorrected for peroxidic oxygen.
‡ Uncorrected for lead introduced by reagents.
I Samarskite from Kothandarama Mine, Nellore District. Analyst: Aswathanarayana, U.
II Samarskite from Sankara Mine, Nellore District. Analysts: Nandi, S. K. and Sen, D. N.[14]
III Samarskite from Nellore: Analysts: Karunakaran, C. and Neelakantam, K.[9,10].
IV Samarskite from Nellore (?). Analysts: Sarkar, P. B. and Sen Sarma, R. N.[16]

A variation graph has been drawn on the basis of analytical values of nine well-known samarskites and the author's results have been plotted on it. The values have been found to be within the expected limits.

TABLE II

	UO_2	ThO_2	PbO	Holme's Formula (Crude Age)	Lawson's Formula (Corrected Age)	Log Formula	Holmes-Lawson's Formula
I	4·62	1·33	0·58	911	856	853	841
II	8·40	1·98	2·25	1976	1739	1726	1687
III	6·93	1·21	2·04	2212	1915	1911	1872
IV	8·68	1·32	2·16	1889	1675	1658	1621

I Sarkar, P. B. and Sen Sarma, R. R. N.[16]
II Karunakaran, C. and Neelakantam, K.[9,10]
III Nandi, S. K. and Sen, D. N.[14]
IV Aswathanarayana, U.

AUTORADIOGRAPHIC STUDIES

An autoradiograph was obtained for a lustrous fragment of the mineral by exposing it for a week. The autoradiograph shows uniform photographic density, which suggests that the mineral has not suffered any alteration or enrichment.

DISCUSSION

Geological Setting

Bain,[1] after a detailed study of some occurrences of radioactive minerals and on the basis of certain theoretical considerations, has formulated the following principles, governing their distribution pattern.

(1) Refractory minerals are distributed rather generally through most crystalline rocks, except those in the centre of the shields.

(2) The centre of the shields is generally free from U-minerals.

(3) The principal uranium metalliferous provinces are on the periphery of shields and in large persistent massifs.

The shield area in India has an extensive spread in the southern Peninsula. "This shield border is fringed with pegmatites containing Uranium-minerals but presents a set of conditions inimical to lodes."

The pegmatites of Nellore District are characterized by concentrated mineralisation in a few favoured localities and diffuse mineralisation in

most. Such a state of mineralisation is naturally incompatible with large-scale development of lodes, which alone are capable of producing a steady and continuous supply of radioactive minerals.

It has been shown that the radioactive minerals of refractory type appear in elongate or orogenic crystalline masses. Bain predicts that no economic deposit can be expected to occur in such a structure even where such places have produced large quantities of columbate-tantalate minerals. Apparently the Nellore occurrence of samarskite and other radioactive minerals fit into this theory well, as the Nellore schist belt is believed to be the schistose facies of elongate Eastern Ghat belt. In point of fact, however, concentrates of samarskite with columbo-tantalates have been reported from a number of mines and it is only the detailed prospecting by geophysical methods including radiometric surveys, that can disclose the actual potentialities, which incidentally will throw some light on the universal applicability of Bain's theory.

Significance of Physical and Optical Characters

The lustrous fragment has a specific gravity which approaches the highest recorded for the mineral and hence may be taken as one of high purity. The relatively low specific gravity of another sample shows that it is slightly altered.

The samarskite specimen examined is massive and isotropic, as almost all the recorded occurrences are, except one that has not been verified. It may be mentioned that this general observation has been satisfactorily explained by the theories of Yagoda[19] and Goldschmidt.[5] Yagoda[19] suggests that the mineral developed originally as an anisotropic crystal and has since become amorphous, possibly as a result of prolonged bombardment of crystal lattice and the recoil of atoms from the decay of uranium and thorium. If this theory were to hold good, every uranium-thorium mineral should be amorphous, which, of course, is not the case. Crystals of radioactive minerals like monazite have been reported from Bihar, Rajaputana, Mysore, Travancore and several other places in the world and similar is the case with thorianite from Ceylon. Goldschmidt's theory[5] appears to explain this anomaly more satisfactorily. From an extensive study of metamict minerals, he concluded that the presence of radioactive constituents is not the primary cause of destruction of the crystal structure but that a re-arrangement of outer electrons takes place in crystals composed of weak acid and weak basic constituents. Thus, minerals like thorianite, monazite and broggerite remain crystalline owing to strong lattice binding despite the high uranium and thorium contents. When the structure is initially weak, as in minerals

containing Nb and Ta, they become amorphous because of degeneration into $Y_2O_3 \cdot Cb_2O_5$. Yagoda's theory of bombardment by radiations together with Goldschmidt's ideas on the weakness of chemical bonds in the Nb-Ta grouping, explains the observed amorphous nature of the samarskite sample.

Formula

Palache *et al.*[15] gave the formula of samarskite as (Y, Er, Ce, U, Ca, Fe, Pb, Th) $(Cb, Ta, Ti, Sn)_2O_6$. According to them it is essentially an oxide (or columbate-tantalate) principally of rare earths, Ca, Fe, U and Th with columbium, tantalum and titanium. " The formula is probably AB_2O_6 with A = Y, Er, Ce, La, U, Ca, Fe″, Pb, Th. B = Cb, Ta, Ti, Sn, W. Water and SiO_2 are usually reported but are believed to be due to alteration and admixture."

Nandi and Sen[14] have recently discussed the formulæ of samarskite given by Rammelsberg, Groth, Doelter, Hess and Wells. The formula that the former[14] have arrived on the basis of analytical data on Nellore samarskite, is similar to the one obtained by Limori and Hata for Korean samarskite, $R_3'' [(Nb, Ta) O_4]_2$, $2 R''' (Nb, Ta) O_4$, $R^{iv} (Nb, Ta)_2O_7$. Nandi and Sen concluded that the samarskite corresponds to a composite salt consisting of two molecules of orthoniobotantalate and one molecule of pyroniobotantalate. The analysis of Glastonbury samarskite by Wells yields a formula $(Y, Er, Ce, La, Di, Ca, Fe^2, Mn, U, Th)_2 (Cb, Ta, Fe, Ti)_5O_{14}$.

Palache and Frondel[15] believe that the difficulties in assigning a formula to this complex mineral are due principally to the uncertainty of the role or iron. The ferric iron, according to them, undoubtedly substitutes for parts of Cb, Ta while ferrous iron probably substitutes for the elements, U, Th, rare earths, Ca and Mn.

The formula worked out by the author on the basis of his analytical data—$Ao \cdot B_2O_5$ where A = Fe, Mn, Ca, Mg, Th, U, Ce, Y; B = Nb, Ta—is similar to the one given by Palache and Frondel. However, it must be said that unless the role of iron is understood, no formula can claim perfection and this formula is no exception. X-ray studies on the distribution of ferrous and ferric iron and autoradiographic studies on the distribution of uranium in the crystal lattice of samarskite, which are proposed to be taken up, may probably lead to some important conclusions on the subject.

Autoradiography

The uniform photographic density of the autoradiograph points out to the conclusion that the samarskite has not undergone any leaching or enrichment.

Age of the Eastern Ghats Pegmatitic Cycle and Archæan Correlation

Holmes, while trying to work out the Archæan succession,[6, 7] pointed out the enormous discrepancy in the ages of Nellore samarskite calculated from the values given by Sarkar and Sen Sarma[16] on one hand and Karunakaran and Neelakantam[9, 10] on the other. He, however, agreed (personal communication to Professor Neelakantam) that the latter value is likely to be nearer to the correct value.

The rationale behind such a conclusion can be easily understood. The Satpura belt, as has been dated by Gaya minerals is 955 ± 40 M.Y. old. All the available geological evidence points out to the fact that the Eastern Ghat belt, whose schistose facies are believed to constitute the Nellore schists, is older than Satpuras. The age given by Sarkar and Sen Sarma[16] to the Eastern Ghats pegmatitic cycle is less than the accurately determined age of the Satpuras and hence unlikely to be correct. The age calculated from the analytical data of Karunakaran and Neelakantam[9, 10] is at least consistent with geological evidence.

Recently Nandi and Sen,[14] while explaining the high lead content of their samarskite specimen when compared with the corresponding value given by Sarkar and Sen Sarma,[16] suggested that the samarskite analysed by the latter might have possibly belonged to the Gaya group of minerals. This suggestion is particularly significant, coming as it does from the colleagues of Prof. P. B. Sarkar, who was the author of the earlier paper and satisfactorily explains the discrepancies.

It appears that the specimens studied by Sarkar and Sen Sarma were not collected by them but were given to them from the G. S. I. collections, soon after the reopening of the museum. These collections were evidently not properly classified and the specimens taken up presumably belonged to the Gaya group, though they were mistakenly thought to have been obtained from Nellore area. The fact that P. B. Sarkar from his later studies on Nellore samarskite gives a value of 1760 M.Y. (quoted by Holmes,[7] as a personal communication from P. B. Sarkar) only confirms the surmise that the apparent discrepancy was due to an unfortunate mistake regarding the locality from which the specimen was collected.

If we exclude the analysis of Sarkar and Sen Sarma, the picture becomes less confusing. The ages calculated on the basis of the rest of the analyses, (Table II) though not same, are at least of comparable order of magnitude. All this data go to show that the Eastern Ghats pegmatitic cycle (1600 ± 50 M.Y.) is undoubtedly older than that of Satpuras (955 ± 40 M.Y.) and

Krishnan's observations in Orissa on the strike directions of Eastern Ghats add weight to this conclusion.

Though Fermor[4] was strongly against the idea of drawing any conclusions on the basis of cutting of the strike lines, he did not disapprove the principle of tentative correlation on the basis of parallelism of strike lines. The strike directions of Eastern Ghats, measured at several places along the east coast by the research workers of the Andhra University Geology Department, is roughly N.E.–S.W. This direction coincides with that of Aravalli belt on one hand and Shillong series on the other and on this basis they may be tentatively correlated. The Aravallis and the Shillong series have not yet yielded any radioactive minerals and hence such a correlation will naturally remain tentative, until sufficient data has accumulated on the ages of pegmatitic cycles of the two formations.

Further Krishnan,[12] while discussing the present state of Archæan correlation, has placed the Shillong Series in the Upper Dharwars. It has also been noted that parts of Shillong series show Satpura strike and as such it will not be surprising if further researches show that parts of Shillong series are Upper Dharwarian and parts lower.

If Eastern Ghats and Aravallis are understood to be of comparable antiquity, Satpuras becomes younger than both—a sequence which Holmes favoured but could not conclusively establish in view of the discrepancy in the ages of Nellore samarskite.

The recently reported occurrence of a radioactive mineral (Allanite ?) in the pegmatites intrusive into the khondalites of Anakapalli area (personal communication of Mr. V. Vijayaramamurthy to Professor C. Mahadevan) is of particular interest to all students of Eastern Ghats, as it is valuable in the solution of the Eastern Ghats continuity problem. Work is in progress on these collections. A mass of evidence[13] has already accumulated to show the contemporaneity of Khondalites, Bezwada gneisses, quartz magnetite rocks and Nellore schists, which constitute the various facies of Eastern Ghats and are believed to belong to the same orogenic cycle. The age of radioactive mineral from Anakapalli will add further information on the subject.

Holmes[7] is now engaged in an attempt to date the monazite occurring in the pegmatites intrusive into the Peninsular gneisses of Bangalore area. The age of the monazite, when interpreted with the age of the Nellore samarskite, will throw some light on Fermor's[3] views on the contemporaneity of Nellore mica schists and the Dharwarian schists of Mysore.

The following tentative correlation is suggested:

Vindhyan

Delhi cycle 735 M.Y.

Satpura cycle 955 ± 40 M.Y. (= Upper Shillong Series ?)

Eastern Ghats cycle 1600 ± 50 M.Y. (= Aravalli ?) (= Upper Shillong ?)

Dharwar cycle

Older gneissic complex

The magnitude of the time-lag between the Satpura pegmatite cycle and the Eastern Ghats pegmatitic cycle clearly suggests that the sequence is incomplete. It is hoped that clearer picture will emerge with the accumulation of some more data on the subject.

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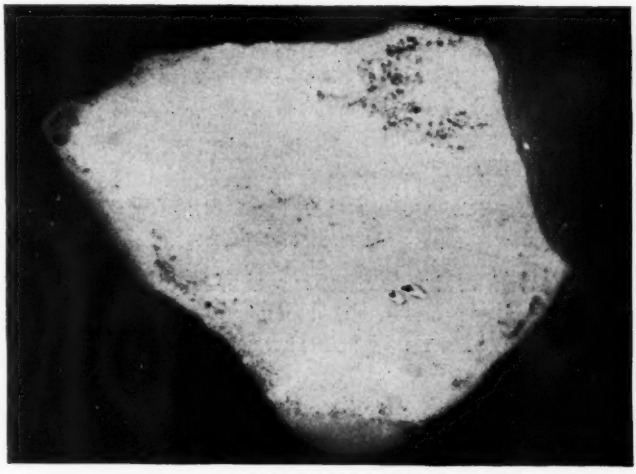
SAMARSKITE



AUTORADIOGRAPH

FLUX DETERMINATION ON HIGH ENERGY PROTONS BY PHOTOGRAPHIC EMULSION METHOD

By D. Lal

(Tata Institute of Fundamental Research, Bombay 1)

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The integral energy spectrum of primary cosmic ray protons with energy below $\sim$ 15 Bev and primary heavy nuclei with energy below 6·8 Bev can be obtained by measuring the flux of all primary cosmic ray particles as a function of latitude. For higher energies, measurements must be based on the result of interactions produced by these primary particles.

The frequency of extensive air showers and the variation with depth of the μ-meson flux underground has been used to obtain the flux of high energy primaries, but the determination of their nature and the estimate of their energy is fairly indirect (Barrett *et al.*, 1952). Interactions of primaries with very high energy have been observed in photographic emulsions. The energy of the primaries causing these interactions can be estimated fairly reliably from kinematical considerations (D. Lal *et al.*, 1952 B) but such events are very rare, which makes systematic intensity measurements difficult. A more suitable method for measuring the flux of energetic primary particles is provided by the socalled emulsion cloud chamber (Kaplon *et al.*, 1952) in which photographic emulsions are alternately packed with brass absorbers and flown at balloon altitudes. Energetic nuclear explosions lead to the production of showers of charged and neutral mesons. The neutral mesons decay into 2 γ-rays in less than 10^{-14} secs. and induce an electron photon cascade in the stack. The growth of the electronic component at various thicknesses of absorber forms the basis of a systematic selection of high energy events. With this technique Kaplon *et al.*, have determined the flux of energetic protons ($E > 4{\cdot}5 \times 10^{12}$ ev) at geomagnetic latitude 41°. This is the only measurement available on the high energy end of the spectrum in which the primary is directly observable. In order to verify their results, and particularly in order to improve the statistics, it seemed desirable to extend this work. We have used an identical arrangement of plates exposed under nearly identical conditions, but at higher latitude ($\lambda = 55°$). We have also chosen a somewhat smaller cut-off value and determined the flux for primaries of energy $E > 1{\cdot}6 \times 10^{12}$ ev.

EXPERIMENTAL

The emulsion stack consisted of a very carefully aligned stack of 20–4″×6″—Ilford G 5 100 μ emulsions on 1·3 mm. glass backing separated by 3 mm. of brass and was flown for 6 hours above 90,000 ft. with emulsion surfaces horizontal.

The effective radiation length for this combination of materials is 2·35 cm. and the geometric mean free path for nucleon interactions is 16·6 cm.

Tracks of heavy primary nuclei were used to obtain accurate alignment of successive plates; this facilitated the subsequent tracing of showers. The design of the stack was such that displacements arising from (*a*) relative rotation of the plates, (*b*) spacing of the plates, and (*c*) tilt of the plates were minimized. The position of a track could be extrapolated within 300 μ in the next plate. The background of tracks makes it difficult to follow with certainty a single minimum ionizing track, but it is sufficient to trace a group of minimum ionizing tracks or a single multiply charged particle.

SELECTION CRITERIA AND SCANNING

The 18th plate (a plate near the bottom of the stack) was scanned-for showers containing within 50 μ at least 4 parallel tracks exhibiting minimum grain density. The observed tracks are in general due to an electron cascade initiated by the decay of neutral π-mesons which have been produced higher up in the stack. The amount of material above this plate corresponds for vertically incident particles to nearly 4 radiation lengths and slightly more than half a geometric mean free path for nuclear interactions.

The observed group of shower particles is then traced back into the preceding emulsions of the stack till one approaches the brass plate in which the primary interaction took place. Here the tracks converge* towards the origin and consist primarily of charged mesons and nucleons produced by a high energy primary. In the emulsion above the brass plate containing the nuclear event no shower is found; frequently the track of the primary can be located in this emulsion, it can always be located if the primary is multiply charged.

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* Occasionally one finds that the number of particles in a shower decreases steadily as one traces the shower into the upper hemisphere and that before its disappearance it consists of only 2 or 4 particles with extremely small angles of divergence. Such showers we have attributed not to nuclear events produced by cosmic ray primaries, but to an electron or γ-ray incident on the stack from the outside.

Energy Estimate of Nuclear Events

The energies of the nuclei responsible for these showers have been estimated in two ways: (i) from the half angle of the cone containing half the shower particles near the nuclear explosion ($\gamma = \frac{2}{\theta_{\frac{1}{2}}^2}$ where γ is the incident energy of the nucleon in terms of its rest mass and $\theta_{\frac{1}{2}}$ is the half angle of the cone), and (ii) from the growth of the soft component as a function of distance from the origin of the shower.

The relation which we used between primary energy and half angle holds if one assumes that the mesons are produced in the cm. system with relativistic energies in a single nucleon-nucleon collision (D. Lal *et al.*, 1952 B). In our case where the nuclear collision occurred in the brass the angular distribution may have been widened by secondary interactions in the same nucleus. This effect is difficult to estimate, but is probably comparatively unimportant at very high energies. By analysing the angular distribution on the assumption of a single nucleon-nucleon collision, we are likely to underestimate the primary energy by an uncertain factor which in every case, is however most probably less than 3.

The total energy carried by the neutral mesons in the forward cone has been estimated by studying the increase in the number of particles at several distances in a cone containing approximately half the shower particles. To make a comparison with theory, we have to estimate the minimum energy of electrons which will stay in this cone; this energy is of the order of 1 Bev, electrons of lower energy being removed from the shower core by scattering. Not knowing the energy spectrum of these mesons we have made the simplifying assumption that we are dealing in the core with monoenergetic γ-rays; the number and energy of photons can then be obtained by comparing the observed multiplication with those calculated according to shower theory (L. Janossy and H. Messel, 1951).

To calculate the incident energy from the total energy carried by photons, the following assumptions have been made:

(1) The cone containing half the shower particles carries approximately 80% of the total energy.†

(2) 25% of the primary energy goes into π°-mesons.

With these assumptions we get agreement between the two energy estimates within about a factor of 2–3.

† Mesons emitted in the backward directions in the C.M. system will appear at large angles and lesser energies and are not considered in these measurements.

THE FLUX OF PRIMARY PROTONS WITH ENERGIES EXCEEDING $1{\cdot}6\times10^{12}$ ev

The stack was exposed horizontally for six hours above 90,000 ft. Eighteen showers were found in an area of 21·5 sq. cm. These numbers refer to showers initiated by a nuclear collision and do not include purely electronic showers initiated by γ-rays incident on the stack. Out of these 18 nuclear showers, two were initiated by α-particles and the rest were produced by primaries of charge $Z < 2$ and are attributed to protons.

A study of zenith angle distributions of the recorded showers indicates a high efficiency of detection between $\theta = 15°$ and 80°. One of the measured shower energies is 9×10^{11} ev, the rest have energies greater than $1{\cdot}6\times10^{12}$ ev. Nearly 50% of these have energies less than 4×10^{12} ev, and we estimate that all showers with energies greater than $1{\cdot}6\times10^{12}$ ev have been detected with a good efficiency.

Assuming geometric interaction cross-section for the incident particles in the stack and an absorption mean free path in the residual atmosphere of 100 g./cm.^{2}‡ and assuming further an isotropic flux at the top of the atmosphere, we find that the integral primary flux of protons per meter^2/sec./steradian ($E > 1{\cdot}6\times10^{12}$ ev) is $\cdot29 \pm \cdot07$. The point obtained from these measurements fits smoothly into the energy spectrum obtained by other experimenters both at higher and lower primary energies. The ratio of protons to α-particles in the same velocity range in this experiment is within statistics equal to the ratio of about 12 found at lower energies.

THE PRIMARY COSMIC RAY SPECTRUM

It has been shown by Peters (1953) that within experimental errors all measurements of the primary proton intensity from 5×10^8 to 10^{16} ev can be represented by the formulæ

$$\log_{10} N_p\,(E) = 6{\cdot}73 - 0{\cdot}0495\,[11{\cdot}9 + \log_{10}(1{\cdot}7 + E)]^2 \qquad (1)$$

where N_p (E) is the number of protons incident per cm.^{2}/sec./steradian whose energy exceeds E Bev. The corresponding curve is shown in Fig. 1 The experimental point at E = 3·5 Bev is that obtained by Perlow in a rocket flight at geomagnetic latitude 41°. The other points for energies E < 15 Bev are values obtained in rocket flights corrected for the contribution of heavy primaries and for the albedo effect of 11% as measured by Perlow. The

‡ Because of the great altitude at which observations were made, the results are not very sensitive to the assumed absorption mean free path.

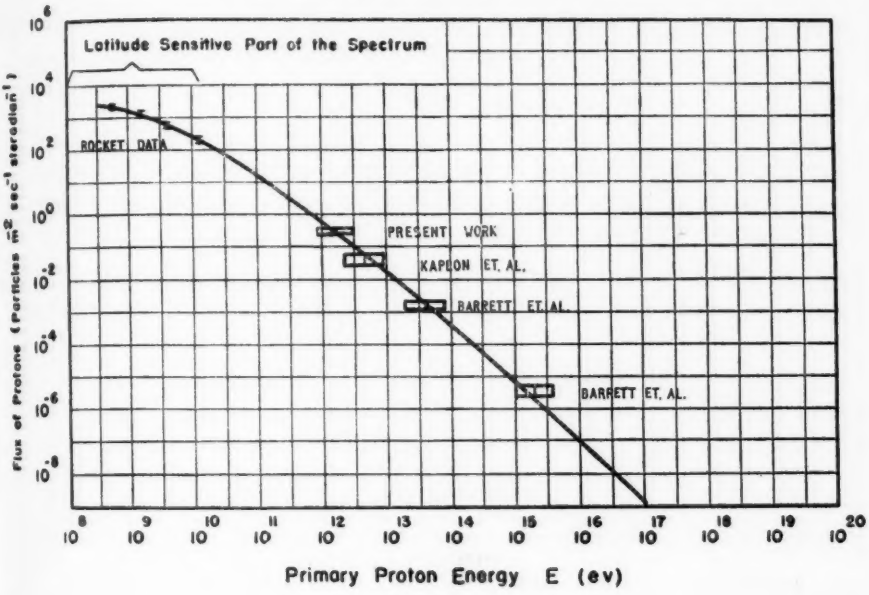

FIG. 1

experimental points at higher energies are those obtained by us and by Kaplon *et al.* as well as those obtained recently by Barrett *et al.* from the intensity of underground mesons and extensive showers. The latter are not corrected for possible contributions from heavier nuclei.

A simple integration of eq. (1) yields the total energy carried by protons of energy larger than E Bev per steradian per cm.^{2} of surface perpendicular to the direction of particles motion:

$$T_p(E) = \int_E^\infty E \frac{dN}{dE}\, dE = \beta\left[e^{-y^3} + \sqrt{\pi}\, a\{1 - \epsilon(y)\}\right] - 1{\cdot}7\, N_p \quad (2)$$

where

$$a = 3{\cdot}41\,; \quad \beta = {\cdot}76$$

$$\epsilon(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^3}\, dx,$$

$$y = 1{\cdot}517\,[6{\cdot}73 - \log_{10} N_p(E)]^{\frac{1}{3}} - 3{\cdot}41.$$

Since as shown elsewhere (Lal *et al.*, 1952 A) the fraction f_A of primaries of atomic weight A is independent of their velocity upto energies of 5×10^{11}

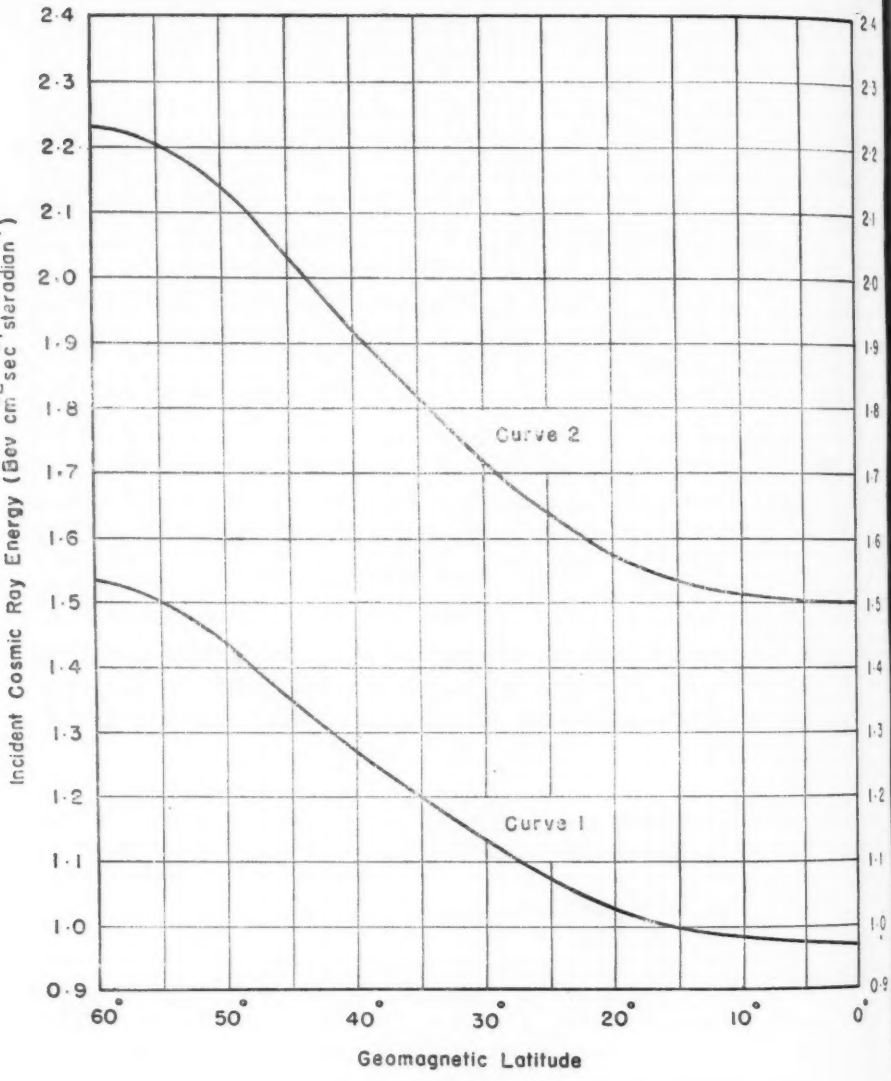

FIG. 2

ev/nucleon, the flux of nucleons of atomic weight A and energy per nucleon larger than E is given by

$$N_A(E) = f_A N_P(E) \qquad (3)$$

where $N_P(E)$ is given by equation 1.

Correspondingly the incident energy due to primaries of atomic weight A and energy *per nucleon* greater than E is given by

$$T_A(E) = Af_A T_P(E) \qquad (4)$$

By inserting for E in equation 2, the cut off value for protons at a given latitude one obtains $T_P(E)$, the flux of incident cosmic ray energy due to protons. The incident energy $T_A(E)$ due to heavy nucleii is obtained from equation 4 by using the cut off value E for heavy nucleii at that latitude.

Curves 1 and 2 in Fig. 2 give the latitude variation of the incident energy due to primary protons and the total primary cosmic ray energy flux respectively at longitude 80° W.

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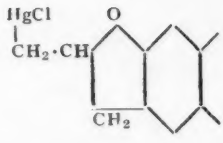
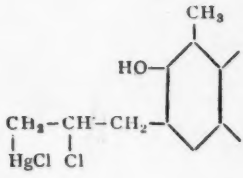
694	Formula II, 	

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